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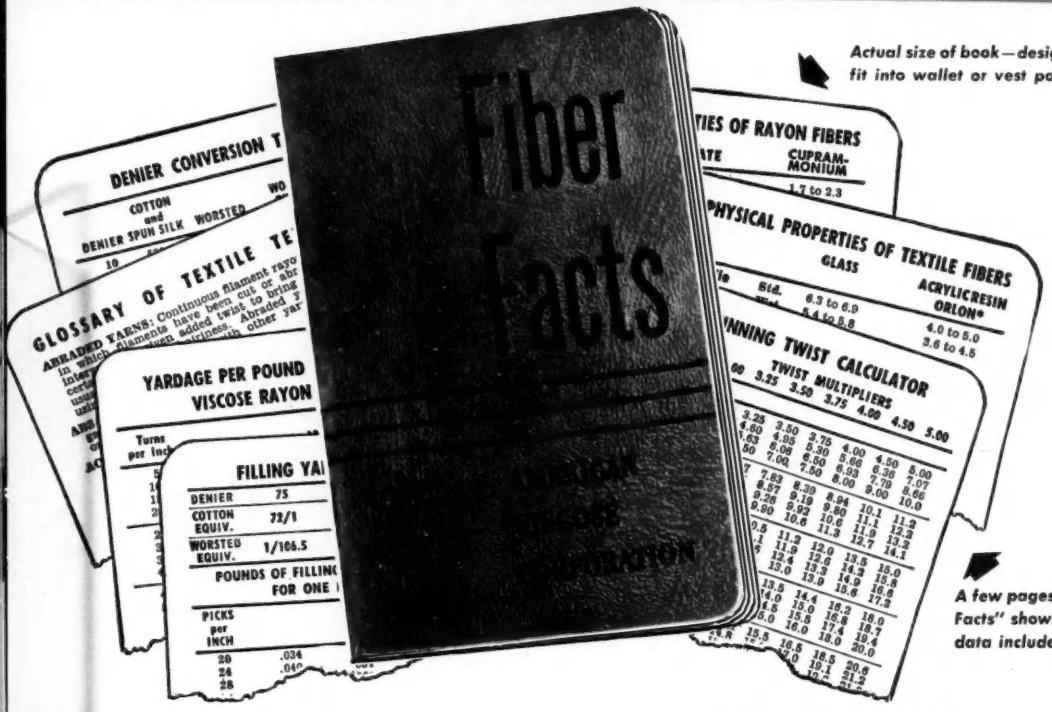

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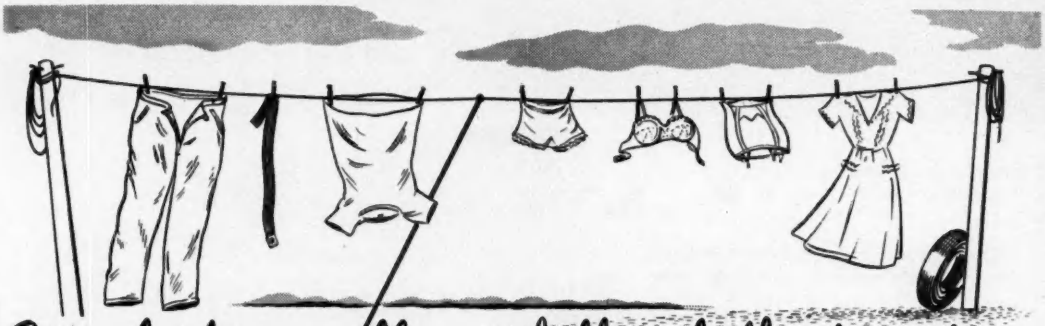

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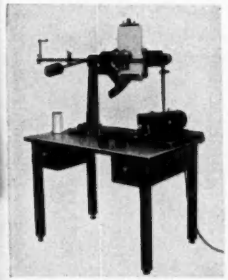

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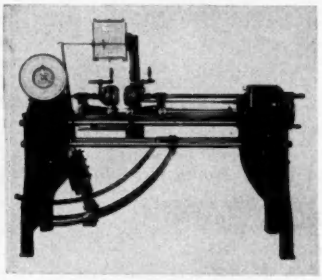

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TEXTILE RESEARCH JOURNAL

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Structural Orientation in Cellulose Acetate Filaments and Its Relation to the Dichroism of Adsorbed Dyes*

D. R. Morey and E. V. Martin

Eastman Kodak Company, Rochester, New York, and Tennessee Eastman Company, Kingsport, Tennessee

Abstract

Factors influencing structural orientation and oriented adsorption of dyes in cellulose acetate filaments were studied using methods based on x-ray reflections and on dichroism. The derivation of a method of computing the percentage orientation from the density of the 002 ring is given. A method for determining the percentage orientation using dichroic dyes is described. In evaluating the data obtained by the latter method, the x-ray data were used as standard.

The dyes examined are classified according to their ability to adsorb directionally on the cellulose acetate substrate. Dyeing conditions affecting results obtained by means of dichroism are discussed in relation to filament structure.

Orientation measurements by both methods were made on continuous-filament yarns drafted to various extensions. The values obtained by the x-ray method were generally higher than those obtained by the method based on dichroism.

Introduction

It has long been recognized that textile fibers are anisotropic in structure, and that there is a close connection between this anisotropy and various mechanical properties. The existence of such anisotropy is manifest in the measurement of a number of quite different properties, such as double refraction, swelling, x-ray reflectivity, and dichroism or polarized fluorescence of adsorbed dyes. Each physical method used to measure anisotropy has its own characteristic emphasis on various aspects of the polymeric structure. Thus, x-ray methods give prominence to the crystalline regions, whereas swelling measurements reflect primarily the state of the amorphous regions.

Polarized fluorescence and dichroism, which arise from the oriented deposition or adsorption of organic dye molecules, reflect not only the character of the polymeric substrate, but also the penetration and adsorption factors which are a part of the dyeing process. An additional factor of interest is the inherent optical anisotropy of the dye molecule itself.

The technique which employs polarized fluorescence has much to recommend it as a means of determining orientation. This is particularly true

* Presented before The Fiber Society at Swamscott, Mass., Sept. 13, 1951.

in the case of cellulosic fibers, for which a number of suitable fluorescent dyes from the direct class are available. In the case of cellulose acetate fibers, however, the number of suitable dyes which fluoresce well is limited; a much larger number of dyes are available for the study of dichroism.

Although dichroism (or polarized fluorescence, which is basically identical in its approach) has been studied and reported to a fair extent on cellulosic materials [5, 10, 15, 20], the published information on its application to cellulose acetate is quite limited. Indeed, reports of the absence of dichroism in cellulose acetate materials are more numerous than reports of its presence. The only positive reports found in the literature are those of Morey [8], who used the emissive, rather than the absorptive, mechanism of the dye, and of Preston, Jackson, and Nimkar [14], who observed dichroism in stretched acetate yarns but not in unstretched yarns.

A study of the technique of making dichroism a quantitative tool in investigations of orientation in cellulose acetate fibers has been carried on intermittently in this laboratory since 1944. Three lots of yarn were used in this work; data which characterize these three yarns are given in Table I. These yarns were drafted various amounts in hot air to produce series of yarns in which the orientation varied over a wide range of values. The T-149 and T-150 yarns were drafted various amounts at one temperature only, whereas the 22459 yarn was drafted various amounts at several temperatures. Orientation in these yarns was measured by the methods of x-rays and dichroism. Some of the results obtained in this investigation are presented herein.

TABLE I. YARN CHARACTERISTICS

Yarn No.	Denier/ no. of filaments	Spinning draft	Tenacity (dry) (g./den.)	Extension at break (dry) (%)
T-149	300/52	0.40	1.30	47.0
T-150	200/52	0.65	1.31	40.6
22459	420/52	0.40	1.37	47.8

The Interrelation Between Orientation Measurements Based on Optics and on X-Rays

The problem of comparing orientation results based on optics and on x-rays has been recognized by Preston and coworkers, as well as by the present authors. The over-all results are in satisfactory agreement, but the two approaches are sufficiently different to require comparison. Preston and Su [15] have recently considered in detail the interrelation of the emissive and absorptive methods, and have shown that the numerical value of an orientation index based on polarized fluorescence is smaller than that of an index based on dichroism; the numerical relation between the two contains an approximation arising from expansions of exponentials. The exact treatment, however, can be obtained readily by the direct approach which is to be described. The basic data from an experiment based on dichroism may be combined in different ways to give different parameters of orientation, each valid in its own right. The treatment first proposed by Preston [13] has much to recommend it, and may be expressed in the form

$$\alpha_D = \frac{\log I_x - \log I_y}{3 \log I_0 - 2 \log I_x - \log I_y} 100, \qquad (1)$$

where I_y and I_x are the transmitted intensities for electric vectors in the y and x directions, respectively, and I_0 is the transmission in the absence of a dye. The same data, however, may be used in the form

$$\alpha'_D = \frac{I_x - I_y}{3I_0 - 2I_x - I_y} 100 \qquad (2)$$

to give a valid index of orientation based on dichroism. These two forms were set up by Morey [9] several years ago. It was pointed out that equation (2) is the form that is analogous to the polarized fluorescence method and the numerical values obtained are lower than those obtained from Preston's form (equation (1)). The two forms differ in that the first is concerned with (resolved) sums of numbers of molecules, whereas the second is concerned with (resolved) sums of numbers of absorbed quanta. In general, the two are not proportional. In other words, there is no difference between the results of polarized fluorescence and dichroism when the corresponding formulas are used. The differences cited by Preston and Su [15] are really due to differences in the means of expressing dichroism.

In comparing the results of experiments based on x-rays and on dichroism, the proper form to use with the method based on dichroism is that first proposed by Preston (equation (1)), since the optical densities are proportional to the concentration, or to the number of dye molecules in (resolved) positions. Similarly, in the x-ray method, which is based on reflections from certain planes in crystallites, the

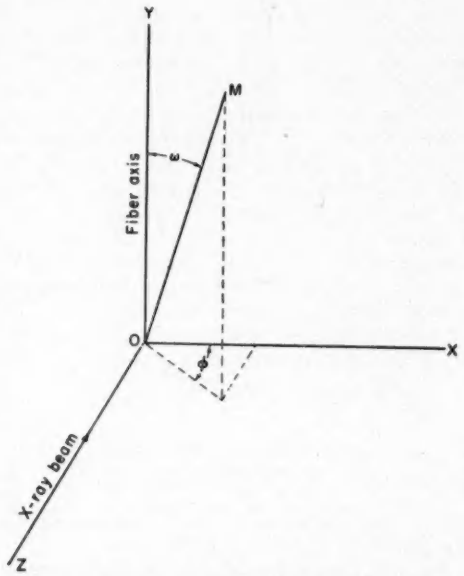


FIG. 1. *Position of the long axis,* OM, *of a crystalline portion chosen at random within the fiber.*

number of crystallites to be found in (resolved) angular positions is sought. In these experiments, both dye and crystallite are characterized by one defining axis, and the resultant effects at the measuring apparatus are directly proportional to the numbers; hence, the orientation index must deal with numbers directly.

The Determination of Orientation by Means of X-Rays

Theory

The qualitative relationship which is known to exist between the length of the 002 arc on a fiber diagram and the orientation is frequently employed to give a ready visual estimate. Various "orientation parameters" based on the shape of the photometer curve have already been set up and used [2, 6, 18].

The method for obtaining the percentage orientation which corresponds exactly to the orientation as expressed by equation (1) is presented here. This method starts with the usual resolution of amplitudes, oriented in three dimensions, onto the XY axes in a plane. (A similar resolution was recently used by Preston and Tsien [17].) In Figure 1, let OM represent the C axis, or long dimension, of an individual crystallite or micellar unit which responds to orienting forces. The angle between this crystallite axis and the fiber axis OY is denoted by ω. The contribution of this particular crystallite to dichroism, assuming that the absorptive mechanism is constrained to the axis OM, is obtained as follows: The projections of OM in the Y and X directions are $\cos\omega$ and $\sin\omega\cos\phi$, respectively. These values correspond to amplitudes, and the squares, $\cos^2\omega$ and $\sin^2\omega\cos^2\phi$, correspond to intensities, either of emission or of absorption. The number of crystallites having angle ω, or lying in the cone of angle 2ω, is proportional to $\sin\omega$, assuming a random distribution of axes OM in space. If the axes OM are not evenly distributed, but show a preferred orientation in the OY (fiber) direction, then this is also a factor in the dichroic effect. Let this distribution be represented by $f(\omega)$. For isotropic material, $f(\omega)$ is simply a constant; this means that in any given small solid angle, centered about any value of ω, the same number of axes OM are found. With oriented material, $f(\omega)$ increases as ω decreases. Since uniaxial orientation is assumed, $f(\omega)$ is independent of the value of angle ϕ.

The Y component of intensity, including all crystallites, is then

$$I_y = \int_0^{\pi/2}\int_0^{\pi/2} f(\omega)\cos^2\omega\sin\omega d\omega d\phi,$$

and the X component is

$$I_x = \int_0^{\pi/2}\int_0^{\pi/2} f(\omega)\sin^3\omega\cos^2\phi d\omega d\phi.$$

Integrating over ϕ,

$$I_y = \pi/2\int_0^{\pi/2} f(\omega)\cos^2\omega\sin\omega d\omega,$$

and

$$I_x = \pi/4\int_0^{\pi/2} f(\omega)\sin^3\omega d\omega.$$

To convert this information into percentage orientation corresponding to the optics of dichroism, the percentage orientation, α, is set up as

$$\alpha_x = 100\frac{2\int_0^{\pi/2} f(\omega)\cos^2\omega\sin\omega d\omega - \int_0^{\pi/2} f(\omega)\sin^3\omega d\omega}{2\int_0^{\pi/2} f(\omega)\cos^2\omega\sin\omega d\omega + 2\int_0^{\pi/2} f(\omega)\sin^3\omega d\omega}. \quad (3)$$

The question of obtaining $f(\omega)$ from x-ray data has already been raised by others [3]. The parameter which coincides with OM is the normal to the diatropic planes, but these planes are not usable because they give very low intensities on the fiber diagram pattern. However, the reflections from the 002 planes (parallel to OM) are strong, and the arc or ring from the 002 planes is usually chosen as the source of photometric data.

There is good qualitative agreement between the density of this ring around its circle and the function $f(\omega)$. Thus, for unoriented materials, a uniform ring is observed, but for a highly oriented material such as ramie, only equator spots are found. The first step, then, in determining $f(\omega)$ consists of the photometric measurement of the 002 ring and the conversion to optical densities. (This involves a knowledge of the proper background intensity to use as I_0, a point to be discussed later. It is also assumed that the exposures are within the linearity range of the film.)

The reason that the density function of the 002 ring, $f_1(D_{002})$, differs from the true $f(\omega)$ may be illustrated by considering the equator position on this ring. The density here is due not only to reflections from 002 planes whose C axes are vertical, but also to reflections from all 002 planes whose normals are horizontal. (The Bragg-angle condition is also satisfied.) These other 002 planes may have their C axes in any direction from vertical to horizontal. Each point on the ring is thus due to a summation of C axes whose directions are not all alike and do not all correspond to the angular position on the photograph. These summations vary with the angle much in the same manner as do the pure components for the same angle, and at the two extremes of perfect orientation and zero orientation, $f_1(D_{002})$ and $f(\omega)$ coincide.

The problem of obtaining $f(\omega)$ rigorously from 002 densities is a difficult one, and is solved only by numerical approximations. Tsien [19] was the first to accomplish this, although Hermans [2] converted 002 densities to an "average" angle of deviation from the axis. Tsien's method is made unduly complicated by inclusion of the Bragg angle in the analysis. This angle is small, being 11° for cellulose and only 4.5° for cellulose acetate, and in the analysis of axial distributions, no significant error is introduced by assuming it to be zero. The method which is presented here for relating $f(\omega)$ and $f_1(D_{002})$ is basically similar to that of Tsien,

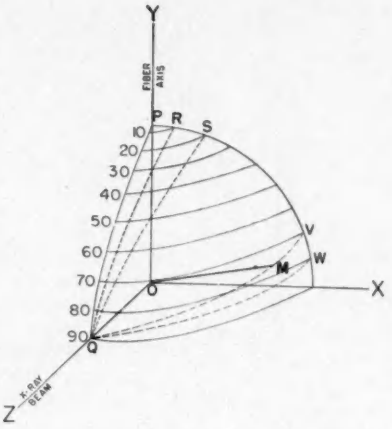


FIG. 2. *An octant of the "locus sphere" for determination of* f(ω).

and is more easily used because of the assumption mentioned.

Figure 2 represents an octant of a "locus sphere" through whose surface pass the long axes of the crystallites. These axes are also imagined to pass through the origin. Thus, $f(\omega)$ represents the number of these axes passing through unit surface of the sphere at angle ω. The sphere is considered to be divided into parallel zones of equal angular width in ω, as shown. (To facilitate the derivation, the locus sphere of Figure 2 is shown divided into zones 10° wide; however, for greater accuracy, 5° zones were used in the actual computations of α_z.) For uniaxial symmetry, the population density, $f(\omega)$, is constant at fixed ω for any position around the axis OY. Within a narrow zone it does not vary much, and it will be reasonable to assume that the average of $f(\omega)$ in such a narrow zone will be given by the value at the middle of the zone. Hence, the average value of $f(\omega)$ between 80° and 90° on the sphere is that at 85°, $f(85)$.

A monochromatic x-ray beam along the OZ axis, incident upon a fiber aligned along the OY axis, gives rise to a diffraction pattern which is ordinarily photographed on a plane parallel to the XY plane. The equator of this pattern is parallel to OX. The equatorial spot on this diffraction pattern is produced by x-ray reflections from all 002 planes (at the Bragg angle) whose axes are located on a great circle cutting OY. For zero Bragg angle, the arc

PQ is part of such a circle, and the spot on the diffraction photograph 10° from the equator is produced by reflections of x-rays from those 002 planes the C axes of which intersect arc RQ. Similarly, the arc SQ corresponds to the spot on the 002 ring 20° off the equator. The last arc shown, WQ, corresponds to all the 002 planes which contribute to the 002 ring density measured at 80° from the equator. This density, which may be called D_{80}, must be proportional to the number of C axes found along arc WQ, and this, as has already been shown, is equal to $f(\omega)$ when $\omega = 85°$. Hence, $f(85) = B \cdot D_{80}$, where B is a constant. The density at 70°, D_{70}, corresponds to arc VQ, which is seen to traverse two zones. Therefore, its value of $f(\omega)$ is

$$\tfrac{1}{2}f(85) + \tfrac{1}{2}f(75) = BD_{70},$$

whence

$$f(75) = 2BD_{70} - BD_{80}.$$

The photographic density at the spot 60° from the equator may be expressed similarly as

$$B \cdot D_{60} = \tfrac{1}{4}f(65) + \tfrac{1}{2}f(75) + \tfrac{1}{4}f(85),$$

whence

$$f(65) = 3B \cdot D_{80} - 2B \cdot D_{70}.$$

Similarly,

$$f(55) = 4B \cdot D_{50} - 3B \cdot D_{80}.$$

In general, if the density on the 002 ring is measured at points $\delta°$ apart, so that $n_0\delta° = 90°$, then the octant of the locus sphere in Figure 2 is divided into n_0 zones each $\delta°$ wide. If these zones are numbered from 1 to n_0, counting from the pole, then the general expression for $f(\omega)$ for the nth zone is

$$f(\omega) = f[(n - \tfrac{1}{2})\delta] = (n_0 - n + 1)B \cdot D_{(n-1)\delta} - (n_0 - n)B \cdot D_{n\delta},$$

or, in a form more convenient to use in actual practice,

$$f(\omega) = f[(n - \tfrac{1}{2})\delta] = BD_{n\delta} + (n_0 - n + 1)B[D_{(n-1)\delta} - D_{n\delta}] \quad (4)$$

This equation contains two terms, one of which is proportional to the density for any particular zone, the other to the difference in densities for adjacent zones. The influence on $f(\omega)$ of the latter term depends very strongly upon the degree of orientation in the yarn. With yarns of low orientation, in which case the difference in densities for adjacent zones is small, $f(\omega)$ is approximately proportional to the density of the 002 ring at the corresponding angle. For zero orientation, the density of this ring is constant. In this case, $f(\omega)$ also is a constant. These facts provide some justification for the use of the data from photometric measurements of the 002 ring directly as a qualitative measure of orientation, as most workers in this field have done. For yarns of high orientation, the difference in density between adjacent zones becomes increasingly important in determining the value of $f(\omega)$. Consequently, it is important in these cases to make the zones rather narrow in order to justify the assumption that the average density in any particular zone is equal to the density at the center of that zone. In this work, the zones were 5° wide.

Data from photometric measurements of the 002 ring can then be substituted in equation (4) to obtain a number which is proportional to $f(\omega)$ for each of the zones. These values of $f(\omega)$ can then be used to calculate the percentage orientation, α_x. Since equation (3) generally cannot be integrated because of the complicated nature of $f(\omega)$, it must be replaced by a summation formula,

$$\alpha_x = 100 \frac{2\sum_0^{90} f(\omega)\cos^2\omega\sin\omega - \sum_0^{90} f(\omega)\sin^2\omega}{2\sum_0^{90} f(\omega)\cos^2\omega\sin\omega + 2\sum_0^{90} f(\omega)\sin^2\omega}, \quad (5)$$

using the numerical values of $f(\omega)$ and ω for each 5° zone.

It should be pointed out that the correct value of α_x, which corresponds to the way in which nature adds dichroic effects, can be obtained only by a summation process which covers the entire angular range. Attempts to select some single "average" angle of orientation [2] to represent $f(\omega)$ lead only to approximations.

Experimental Procedure

In determining the densities on the 002 ring, a microphotometer is needed. The densities must be computed with due allowance for the background blackening caused by general scatter, because the value of α_x is quite sensitive to the value adopted for I_0. This is a problem which has been recognized by other workers, and various methods for determining the background density have been used. The difficulty comes about because the background decreases from the center of the film toward the edges, and it is the value at the ring position which is desired but is not directly measurable. Sisson

and Clark [18] have measured the background on the lightest portion of the film between the 002 arc and the next arc of larger diameter. Ingersoll [6] has chosen as background the minimum intensity between the 101 and $10\bar{1}$ arcs at 45° from the equator line, having found this to improve the agreement between measurements based on the 101 and 002 arcs.

An alternate technique is to make a photometer trace radially through the center, the different interferences thus appearing as peaks on the curve. This technique was used by Hermans, Kratky, and Platzek [3], and the background was obtained by drawing a line, with visual judgment, which appears to separate the reflection peaks from their general base line.

The problem of background correction has been discussed in considerable detail by Hermans and Weidinger [4]. These authors started with a radial trace and again interpolated what appeared to be the best base line to fit the peak curvatures. They noted the separate contributions to background of amorphous material and air, as well as Compton and thermal scatter.

In the present work, two methods for estimating background density were used, and both gave satisfactory results. In the first, the densities at two points bracketing the ring distance and on a line 90° to the equator were averaged. The two points selected were at $0.6X$ and $1.67X$, where X represents the distance from the central spot to the mid-point of the 002 reflection. This method was later replaced by that of Hermans, Kratky, and Platzek [3], using radial microphotometer curves and drawing in the estimated background. The two methods gave essentially identical values of background density. Estimates of background density from the radial microphotometer curves taken at 90° to the equator could usually be made with an uncertainty of about 0.01 in density units. Change in background density of this amount produces a change in α_z of about 3.5% of the value of α_z throughout the range observed in the present work.

Results

In Figure 3, which shows the interrelationship of drafting temperature, percentage stretch applied to the yarn, and orientation, the strong dependence of orientation upon drafting temperature is apparent. At low drafting temperatures, the relatively high tension produced in the yarn resulted in fairly good alignment of the ordered regions in the fibers. As the temperature increased, the yarn became more plastic, and the tension during stretching was reduced; consequently, for a given percentage stretch, the degree of orientation obtained was lower.

Data on orientation, breaking stress, and extension at break for three series of yarns drafted at constant temperature are shown in Figure 4. In all three cases, orientation increased rapidly at low percentages of stretch and appeared to approach a maximum at the higher values of stretch. The breaking stress and extension at break show the expected correlation with orientation. It is of interest that at the highest values of percentage stretch the breaking stress diminished. This fact indicates that tension on the yarn during the drafting process exceeded the optimum value and that internal ruptures were produced in the filaments.

The Determination of Orientation by Means of Dichroic Dyes

Theory

Once the orientation behavior of a known series of yarns has been established by the x-ray methods just described, these "calibrated" specimens may be used to explore the use of dichroic dyes as tools for studying arrangement in the polymer mass. Such a use depends upon three basic assumptions which have been generally recognized:

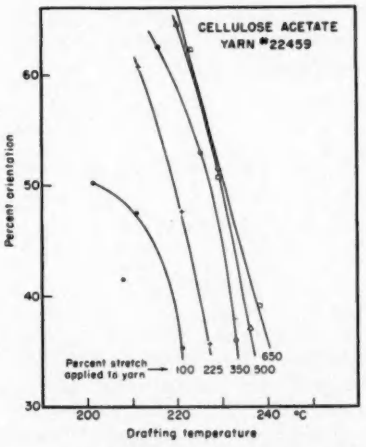


FIG. 3. *Relationship of percentage orientation in cellulose acetate yarn No. 22459, as determined by the x-ray method, to drafting temperature.*

(*a*) The dye molecule itself is essentially dichroic; its absorption mechanism is essentially that of a linear oscillator.

(*b*) The deposition of the dye within the fiber takes place under the influence of adsorptive forces which align the dye spatially in a direction having a direct correspondence to some structural direction of the polymer substrate.

(*c*) Within the dye molecule, the axis corresponding to the linear oscillator is essentially parallel or perpendicular to the axis defining its attachment or adsorption to the polymer substrate.

The simultaneous validity of these assumptions is proved only by going through the actual procedure of dyeing a series of yarns, making measurements of dichroism, and combining the measurements according to equation (1). These assumptions show the reasons why the phenomenon is not observed in some cases. It is possible, however, to test assumption (*a*) independently by using a polarizing microscope to examine crystals of the pure dye for dichroism. The structural formula also gives a method of prediction because dyes possessing rodlike structures tend to show marked dichroism.

The observed dichroism is thus a function, first, of the dye chosen, and, second, of the fiber structure which is accessible to the dye. The most accessible surface is, of course, the skin; next are the walls of capillaries and pores; and, finally, the internal micellar surfaces, which, with proper swelling, may serve as adsorbing surfaces. Thus, the state of dispersion of the dye and the swelling power of the dye bath are also variables.

Experimental Procedure

A number of parallel strands of cellulose acetate yarn are wound on an aluminum frame containing a central hole for the examining light to pass through. Figure 5 is a photograph of a mechanical winder which winds six frames at a time. The traverse can be adjusted for a given denier, so that the threads just touch to form an even layer. One layer may be wound over another when desired.

These frames, with undyed yarn wound upon them, are then transferred to a rack which is rotated in the solution of dye. This assembly is shown in Figure 6. After the packet of yarn is dyed and air-dried, it is placed in a glass cell (also shown in Figure 6); the cell is then filled with decahydro-

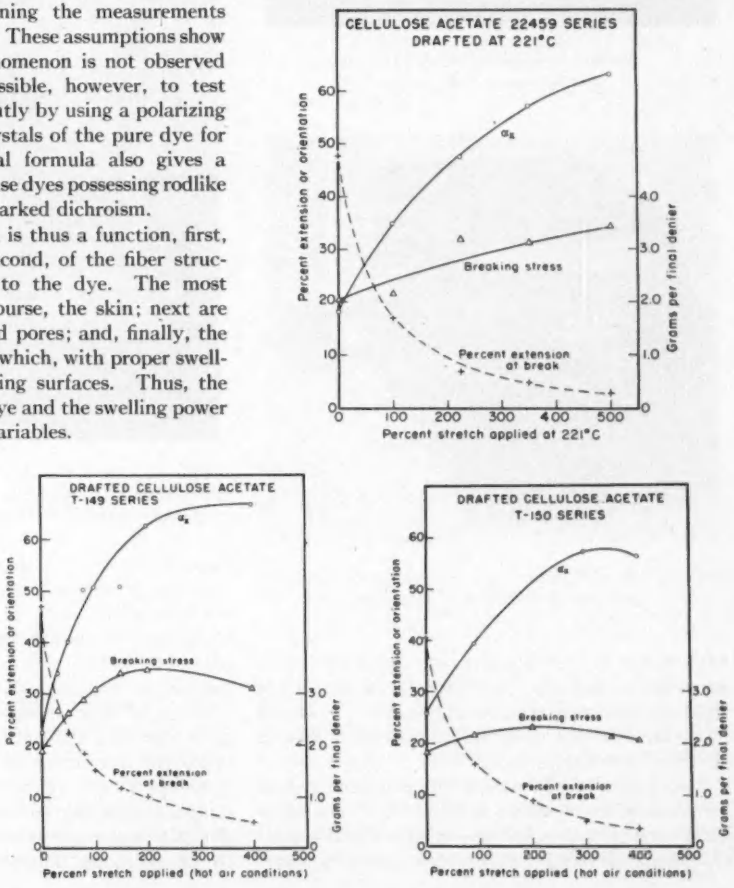

CELLULOSE ACETATE 22459 SERIES
DRAFTED AT 221°C
Percent extension or orientation
Grams per final denier
Breaking stress
Percent extension at break
Percent stretch applied at 221°C
DRAFTED CELLULOSE ACETATE T-149 SERIES
Percent stretch applied (hot air conditions)
DRAFTED CELLULOSE ACETATE T-150 SERIES
Percent stretch applied (hot air conditions)

FIG. 4. *Relationship of breaking stress, extension at break, and percentage orientation obtained by the x-ray method to the stretch applied at constant temperature for three series of yarns.*

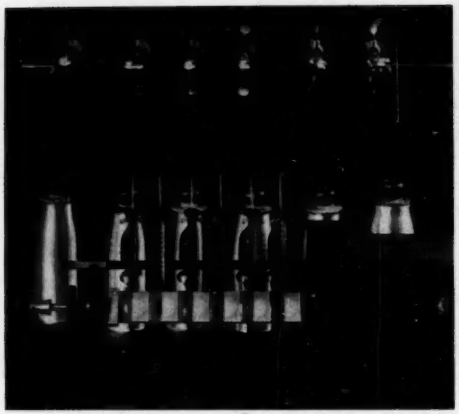


FIG. 5. *Machine for winding packets of yarn for use in measurements of dichroism.*

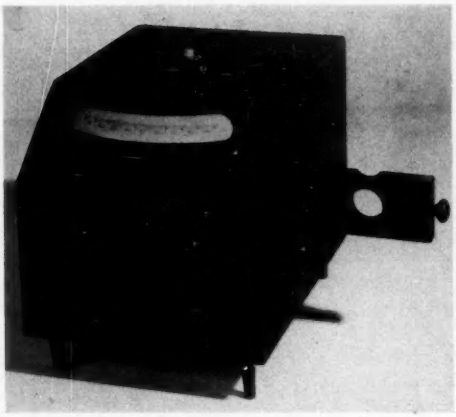


FIG. 7. *The dichrometer used for making measurements of degree of dichroism in dyed yarns.*

naphthalene. This liquid has a refractive index very close to that of acetate yarn; hence the surface reflections and scattering are eliminated. It should be mentioned that care must be taken to remove air trapped in the yarn.

The apparatus for making the measurements of light absorption is shown in Figure 7. This apparatus consists of (1) a voltage-regulated light source; (2) a beam of parallel light which passes, in order, through a color filter, the sample, a polarizing sheet, and onto a barrier-layer photocell; and (3) a galvanometer and shunt, to read the output from the photocell. The polarizing sheet and photocell are mounted together and may be turned as a unit to the proper positions to measure the amount of transmitted light polarized parallel and perpendicular to the yarn filaments. A cell holding a packet of undyed yarn immersed in decahydronaphthalene is placed in the beam to obtain I_0. The dyed sample is then moved into the beam of light, and the galvanometer response at the two positions of the photocell and polarizer is noted.

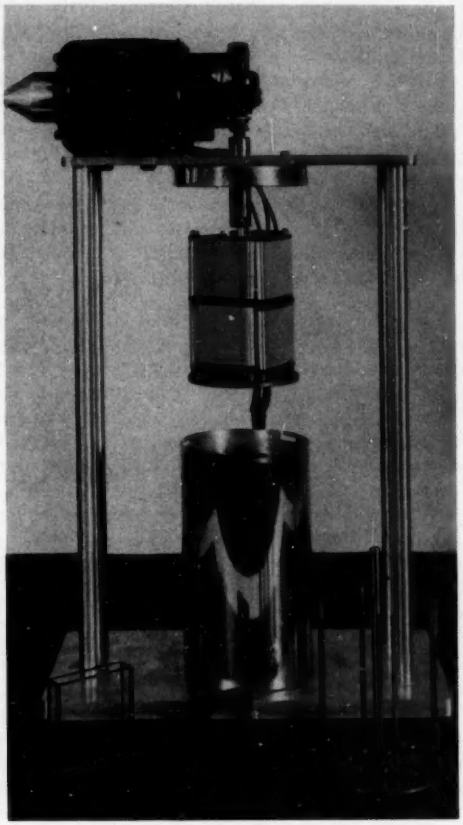
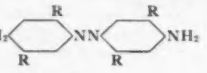
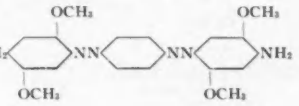


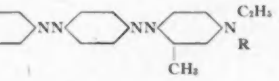
FIG. 6. *Apparatus for dyeing packets of yarn for measurements of dichroism; and a glass cell for holding the packets in the dichrometer.*

TABLE II. EXPERIMENTAL DYES SHOWING A HIGH DEGREE OF DICHROISM ON CELLULOSE ACETATE YARN

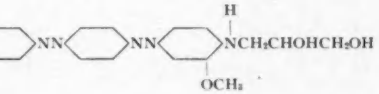
(2a)


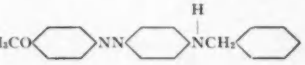
R = H or OCH_3

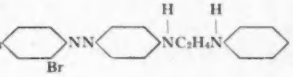
(2b)


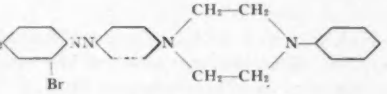
(2c)


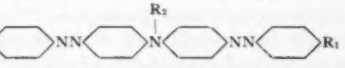
R = CH_2CONH_2 or $CH_2CHOHCH_2OH$

(2d)


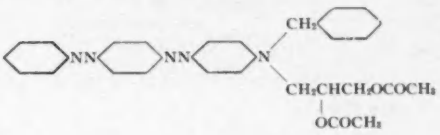
(2e)


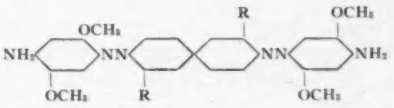
(2f)


(2g)


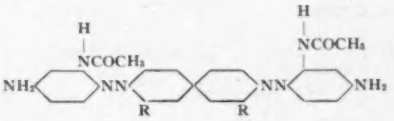
(2h)


R_1 = NO_2, R_2 = H; or R_1 = NH_2, R_2 = C_2H_4OH

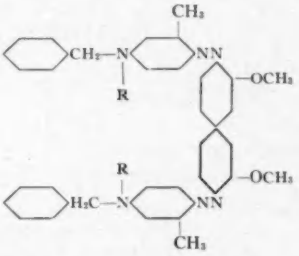
(2j)


(2k)


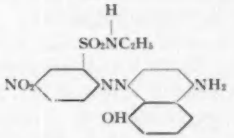
R = H or OCH_3

(2l)


R = H or OCH_3

(2m)


R = H or C_2H_4OH

(2n)


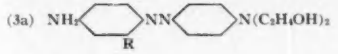
(2o)

The light used must be limited in wave length to approximately the middle of the absorption band of the dye selected. In the apparatus of Figure 7, this is accomplished by means of a number of glass filters selected for transmission of reasonably narrow bands. These filters are mounted in a disc which rotates the desired filter into the beam of light.

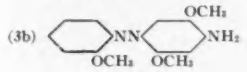
Results

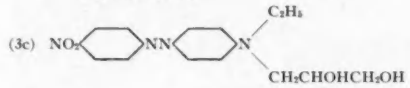
A survey of dyes themselves, using a standardized dyeing procedure and standardized cellulose acetate yarn, is one of the necessary steps in the determination of orientation by means of dichroic dyes. Table II lists some experimental dyes which have been found to exhibit pronounced dichroic effects

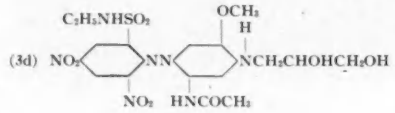
TABLE III. EXPERIMENTAL DYES SHOWING A MEDIUM DEGREE OF DICHROISM ON CELLULOSE ACETATE YARN

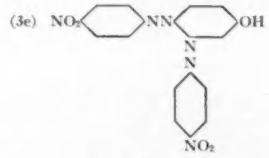
(3a) 

R = H or Cl

(3b) 

(3c) 

(3d) 

(3e) 

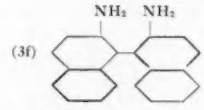
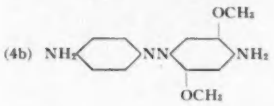
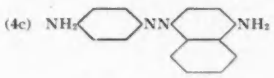
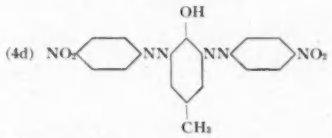
(3f) 

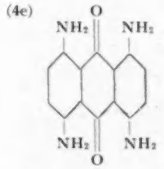
TABLE IV. EXPERIMENTAL DYES SHOWING A LOW DEGREE OF DICHROISM ON CELLULOSE ACETATE YARN

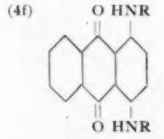
(4a)

(4b) 

(4c) 

(4d) 

(4e) 

(4f) 

R = H or C_2H_4OH

on cellulose acetate yarn. Tables III and IV list those experimental dyes which showed only intermediate and very low dichroism, respectively. A similar classification of certain commercially available dyes is presented in Table V. A comparison of the structure of dyes listed in Tables II, III, and IV shows that those dyes possessing an elongated and symmetrical form are more likely to exhibit dichroism on yarns than those dyes possessing dissymmetry, shortness, and unbalanced shape. Similar considerations determine whether or not dichroism is shown by substantive dyes on cellulosic fibers [7, 21].

Dissymmetry, shortness, and unbalanced shape may reduce the observed dichroism in any of several ways: (1) by furnishing a nonlinear absorbing mechanism; (2) by exhibiting more than one absorbing mechanism, the different mechanisms having different directional positions in the molecule; and (3) by causing adsorption or attachment of the dye molecule with its absorbing axis out of line with the fiber axis. The third mechanism is the most common one in cases of low dichroism [12].

The conditions of dyeing also affect the observed dichroism through the following factors: (1) amount of swelling of the fiber; (2) state of dispersion of the dye; (3) mode of adsorption (as by use of a mordant); and (4) use of a developer.

The dye bath used affects the degree of swelling of the fiber and the dispersion of the dye. For example, Solacet Fast Crimson BS and Methylene Blue both showed considerably less dichroism when applied to the yarn from an aqueous dye bath than when applied from a 1:1 (by volume) ethanol-water mixture.

An example of the effect of a developer is furnished by experimental dye No. 4b (Table IV), which is

TABLE V. DICHROISM SHOWN BY SOME COMMERCIAL DYES ON CELLULOSE ACETATE YARN

High	Medium	Low
Eastone Rubine R	Eastone Scarlet BG	Eastone Orange 2 R
Eastone Red B	Eastman Violet 5 RLF	Eastman Fast Yellow 4 RLF
Eastone Blue BB	Eastman Blue BNN	Eastman Fast Yellow GLF
Gallo Blue	Basic Fuchsin Y	Iodine (using KI-I_2 solution as dye bath)
Solacet Fast Yellow GS	Solacet Brilliant Blue BS	
Solacet Fast Scarlet CS		
Solacet Fast Crimson BS		
Methylene Blue		

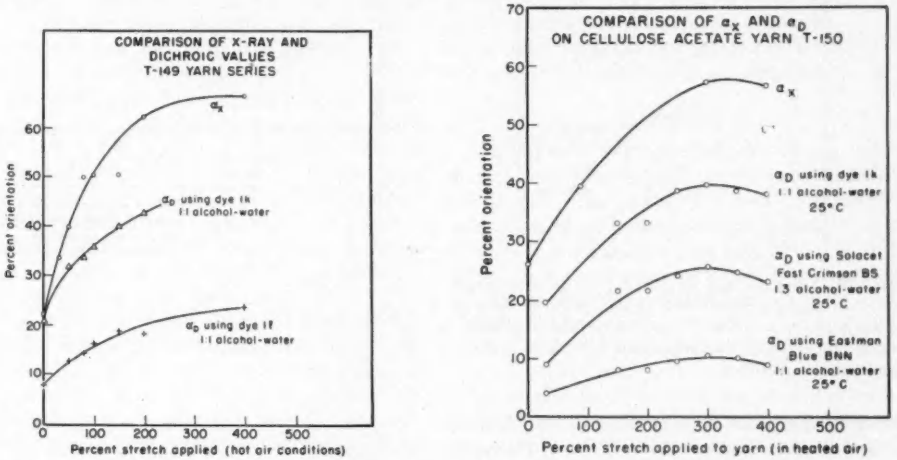

COMPARISON OF X-RAY AND DICHROIC VALUES T-149 YARN SERIES
Percent orientation
Percent stretch applied (hot air conditions)
COMPARISON OF α_X AND α_D ON CELLULOSE ACETATE YARN T-150
Percent orientation
Percent stretch applied to yarn (in heated air)

FIG. 8. *Relationship of x-ray (α_x) and dichroism (α_D) values of orientation to percent stretch applied to the yarn for two series of yarns.*

Note: Dyes 1k and 1l correspond to dyes 2k and 2l, respectively, of Table II.

identical with dye No. 2a, but which upon development with 3-hydroxy-2-naphthoic acid no longer showed marked dichroism.

The case of Congo red is particularly interesting in showing, by dichroic measurement, an orientation of some 15% for both low-draft and high-draft yarns. Since x-ray measurements indicated that the latter yarn was much more highly oriented than the former, it must be concluded that Congo red is not following the internal structure of the yarn; this is in agreement with its being substantive for cellulose only. The external parts of the fiber which this dye is following apparently do not change orientation as the fibers are stretched. This recalls the dichroism shown by depositions of silver and other metals within pores whose shapes are elongated in the fiber direction [1, 11].

The percentage orientation as measured by dichroism of adsorbed dyes would be expected to be less than that obtained from x-rays, and this is

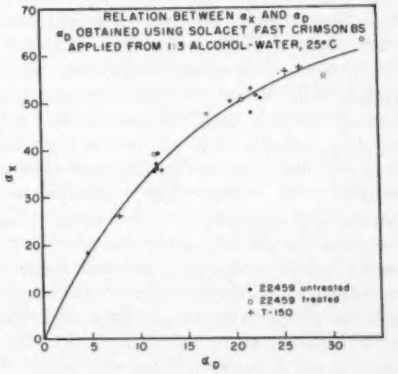
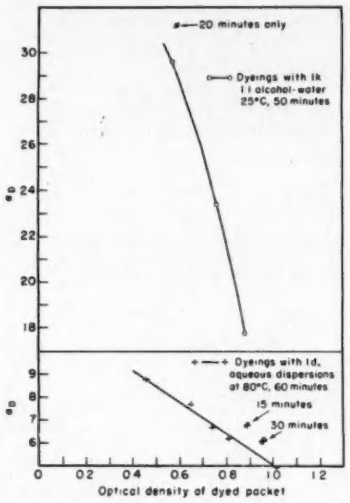
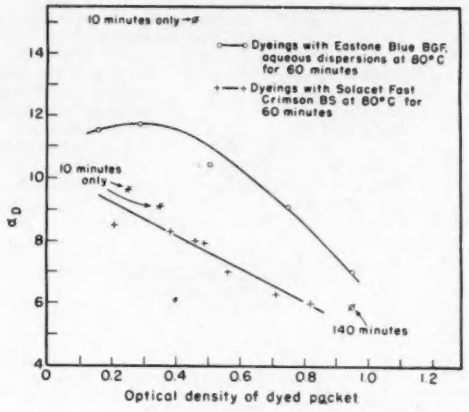


FIG. 9. *Relationship between x-ray (α_x) and dichroism (α_D) values of orientation for two series of yarns. (The treated yarns were subjected to the regular dyeing procedure, but without dye, before the x-ray measurements were made.)*





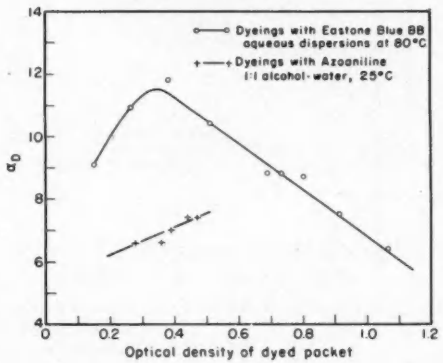

Dyeings with Eastone Blue BB
aqueous dispersions at 80°C
Dyeings with Azoaniline
1:1 alcohol-water, 25°C
Optical density of dyed packet

FIG. 10. *Relationship of the degree of orientation obtained by using dichroic dyes to the optical density of the dyed packet.* a—*Above.* b—*Above, right.* c—*Right.*
Note: Dyes 1d and 1k correspond to dyes 2k and 2l, respectively, of Table II.

found to be the case. As is well known, the method of x-rays measures only the orientation of the well-organized crystallites. The adsorption of dichroic dyes, however, is dependent upon all phases of the structure, including both crystalline and amorphous portions, as well as upon external and internal surfaces available to the dye. The weight given to each phase depends upon such factors in the dyeing procedure as concentration and degree of dispersion of the dye, and temperature and concentration of the dye bath. Figures 8 and 9 show that, using suitable dyes, dichroism does have a definite correlation with the degree of orientation as measured by x-rays. The method based on dichroism is thus established as a valid, quantitative method for use on acetate yarns. The actual numerical values of α_D are lower than those of α_x, as is expected. The lower values of α_D indicate the presence of poorly oriented amorphous material.

It has been shown in Tables II–V that the dye molecule itself is important for the value of α_D. However, starting with a dye which itself is intrinsically dichroic, the effects of the dyeing procedure itself may be followed. This is illustrated in Figure 10a, which shows the results of varying the concentration of dye in the bath. The amount of dye taken up may be followed by the optical density of the dyed packet, as measured in the apparatus of Figure 7, but using unpolarized light or summing the horizontally and vertically transmitted components.

Figure 10a also shows that as more and more dye is taken up, the over-all value of α_D decreases rapidly. Hence, it may be concluded that, for the conditions shown, the dye which goes on first is taken up by the most highly oriented structures or surfaces, and that the succeeding dye is taken up by the more random portions. Preston and Tsien [16] came to a similar conclusion in a study of viscose rayons. This conclusion is at variance with the usual idea that the crystalline regions are the least accessible, and that the amorphous and disordered parts are the first to be exposed in a swelling process. But it must be kept in mind that it is not the interior of crystalline regions which are being

dyed; it is only their surfaces, which are accessible through the micropores and channels which lead to them. Further evidence that the most accessible surfaces are also the best oriented is obtained from the results of the experiments at different dyeing times. The same yarn, dyed to the same depth but in less time, showed an increase in the value of α_D (see Figure 10a). Also, when the dyeing time was 140 min. instead of 60 min. (see Figure 10b), the dye was able to penetrate the less-accessible regions which are more randomly oriented; therefore, the value of α_D dropped below the value obtained for 60-min. dyeing.

Preston and Tsien [16] observed a similar effect in viscose rayons dyed with dichroic dyes. They ascribed the higher values of dichroism obtained when shorter dyeing times were used to the existence on the surface of the filament of a highly oriented skin which was dyed first. Although the evidence for such a highly oriented skin on viscose rayons is good, dry-spun acetates have not been shown to have this type of skin. The sharp drop in α_D obtained when the dyeing time was the same but the density was increased may also have been caused by a build-up of dye in layers more than one molecule thick. It is reasonable to suppose that the succeeding dye layers were less able to follow the orientation of the polymer substrate. Preston and Tsien [16], who made calculations on the available internal surface and the available dye in connection with their experiments on viscose, were inclined to discount this explanation. However, their calculations do not recognize that multimolecular adsorption may be proceeding in some areas before others have even taken on the first layer of dye.

Figure 10c shows an anomalous effect: α_D initially rose with increasing concentration of dye, reached a maximum, and then diminished. The initial rise in α_D appears to be at variance with the idea that the most easily accessible regions are the best oriented. This difficulty may possibly be resolved by the following considerations: At very low concentrations, the dye is well dispersed and therefore is able to penetrate small pores in the filaments and adsorb on most, if not all, of the internal surfaces. This results in a relatively low value of α_D. At somewhat higher concentrations, the dye particles are larger and therefore are able to penetrate only the larger channels in the swollen filaments. Under these conditions, the regions of the yarn which are most easily accessible to the dye are also the best oriented. Therefore, the maximum value of α_D is obtained. At still higher concentrations, multilayer adsorption of dye occurs, and lower values of α_D are obtained. Additional evidence that the state of dispersion of the dye and distribution of sizes of pores in the swollen filaments are important factors in this process is furnished by the effect on α_D of type and temperature of dye bath. Particularly marked was the effect obtained with Eastone Blue BB. Using a 1:1 (by volume) alcohol-water bath at room temperature, the value of α_D was one-fifth of the value obtained using a water bath at 80°C.

Summary

The structural orientation of cellulose acetate filaments has been studied to determine its relation to the dichroism of adsorbed dyes. The methods used to study this relationship were based on x-ray reflections and the use of dichroic dyes. In evaluating the data obtained by the latter method, the x-ray data were used as standard.

The dyes examined may be classified according to their ability to adsorb directionally on the cellulose acetate substrate. Those dye molecules which have an elongated, symmetrical structure tend to show higher degrees of dichroism than those dyes having a short, unsymmetrical, or unbalanced structure.

The percentage orientation value obtained by the method of dichroism is markedly affected by the composition of the dye bath, presumably by means of its effect upon the degree of dispersion of the dye and upon the amount of swelling of the fibers. When dyes were applied from a mixture of ethanol and water, they often showed very different dichroism than when applied from a purely aqueous medium.

In most cases, the percentage orientation measured by dichroism decreases with increasing optical density of the packets. This fact indicates that those regions of the fibers which are most easily accessible to the dye molecules are also the most highly oriented. However, this effect may also be due, at least partially, to multilayer adsorption, since layers of dye succeeding the first layer would probably be increasingly less able to follow the structure of the cellulose acetate substrate.

In general, the method of dichroism yields lower values of orientation than the method of x-ray reflections, indicating that the former takes amor-

phous material into account. When use is made of certain selected dyes and dyeing procedures, however, there is a high degree of correlation between the results obtained by the two methods.

Acknowledgment

Substantial assistance has been rendered by a number of workers who have been associated with this project. It is a pleasure to acknowledge in particular the contributions of Messrs. D. H. Baker, Russell Ferrey, Wilbur I. Kaye, Michael Susko, John W. Tamblyn, and John F. Whitney.

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Modification of Wool with *Beta*-Propiolactone*

Part I: The Chemistry of the Reaction

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IN THE COURSE of investigations of the effects of chemical modification on the useful properties of wool, it has been found that treatment with *beta*-propiolactone results in considerably altered chemical and physical properties. The modified wool is softer and whiter than untreated wool and has somewhat greater luster. A particularly interesting result is marked alteration of felting properties. Through suitable treatment, felts are obtained that have high split-resistance and tensile strength [16]. The felting and mechanical properties of propiolactone-treated wools will be described in subsequent publications; in the present paper are considered the chemical aspects of the interaction of *beta*-propiolactone with wool.

beta-Propiolactone, $CH_2—CH_2$ / $O——CO$, is a moderately high-boiling (92°C/100 mm.), water-white liquid which has been known since 1915 [15] but has only recently become available on a commercial scale [17]. The literature reveals no studies of the interaction of *beta*-lactones with proteins, although the somewhat analogous reaction with epoxides is well

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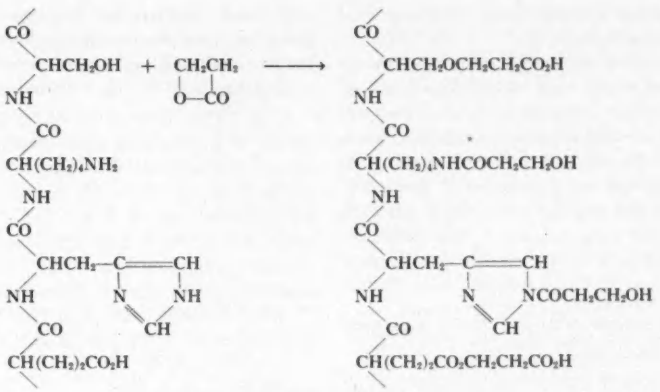
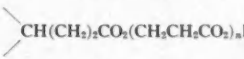


known [4, 5]. In view of the known reactivity of *beta*-propiolactone with such compounds as phenols [10], carboxylic acids [9], alcohols [11], and amines [7] and the fact that these and other reactive groups are present in the wool-protein side-chains, *beta*-propiolactone might be expected to react with wool at these sites. For example, reaction with serine, lysine, histidine, and glutamic acid residues on the protein polypeptide chain might be as shown above.

As reported in the references cited above, alkyl-oxygen opening for hydroxyl (under neutral conditions) and for glutamic acid is assumed; an acyl-oxygen opening is assumed for the amines. Since such reactions generate further reactive centers, we expect additional reaction to occur—*i.e.*, polymerization may follow. In this way the glutamic acid residue, for instance, might give



In addition to such an "anchored" polymerization, some simultaneous formation of polyester acids [8] on the fiber surface might be anticipated.

Conditions of Treatment

Regardless of the nature of the reactions involved, total nitrogen analysis provides a convenient measure of the extent of modification. As illustrated in Table I, the accrued weight, on a dry basis, is satisfactorily accounted for by the decrease in total nitrogen content—that is, no nitrogen is gained or lost during reaction. The wool samples were dried and weighed, submitted to propiolactone modification as described below, dried and reweighed, and analyzed for nitrogen by the Kjeldahl method.

The values compared are identical, within the accuracy of the nitrogen analyses. If the small difference is significant, it might be ascribed to transfer loss or to solubility of the wool or impurities.

In preliminary studies of the reaction of propiolactone with wool, ether was used as a solvent for the lactone, and it was observed that at ordinary temperatures virtually no reaction occurred with air-dry (65% R. H.) wool or with wool which had been thoroughly oven-dried. Prior soaking with anhydrous solvents such as alcohol and benzene, however, induced reaction with lactone. It was subsequently observed that reaction occurred with air-dry wool when carbon tetrachloride was used as solvent for the lactone. In all cases it was necessary to use separate controls, since the time and extent of solvent pretreatment are very important in determining the extent of reaction. This dependence may be due to the sensitivity of the reaction to the moisture content of the wool, to traces of polymerization catalysts, or to the extent of swelling induced by prior solvent treatment. Since the propiolactone reacts first with the amorphous portions of the wool protein, it seems probable that swelling is the important factor. An apparently analogous effect of preswelling on the

TABLE I. COMPARISON OF WEIGHT INCREASE WITH NITROGEN ANALYSES

Sample	N (%)	N calculated from weight increase (%)
Control	16.6	—
1	8.15	8.22
2	8.96	9.00

acetylation of cotton with ketene has been reported by Hamalainen and Reid [12].

An extended series of modification treatments was carried out to study such variables as temperature, solvent, lactone concentration, and mode of drying. In all cases the wool, in loose carded form, was immersed in the solution and shaken occasionally during the period of treatment. At the end of the reaction time the samples were rinsed with the lactone solvent and water-washed. The propiolactone* was stored before use at 4°C to prevent polymerization.

* The authors are indebted to the B. F. Goodrich Chemical Company for a sample of this material.

Table II gives total nitrogen percentages and corresponding percentage uptakes of propiolactone for various times and conditions of treatment.

The data lead to the following conclusions:

1. At 21°C air-dry wool (65% R.H.) reacts very slowly, if at all, with aqueous solutions of propiolactone (experiment 1). This is not surprising, for under these conditions the lactone hydrolyzes, with a half-life of about 3 hrs. [2]. Reaction in dry ether or benzene is also negligible under these conditions (experiments 3, 5, 36). Reaction occurs, however, in dry carbon tetrachloride (experiment 7), or in benzene containing sufficient carbon tetrachloride to solubilize the lactone (experiment 6),

TABLE II. PROPIOLACTONE-MODIFIED WOOLS

Expt. No.	Pretreatment[1]	Solvent	Time	Lactone conc. (%)	Lactone-to-wool ratio[2] (g./g.)	Temp.[3] (°C)	Total N[4] (%)	Uptake of propiolactone (%)
Wool No. 1[5]							16.6	
1	None[6]	H_2O	48 hrs.	3.00	3.00	21	16.26	2.1
2	EtOH, CCl_4	H_2O	48 hrs.	3.00	3.00	21	16.11	3.0
3	None	Et_2O	48 hrs.	3.00	3.00	21	16.80	(−1.2)
4	EtOH, CCl_4	Et_2O	48 hrs.	3.00	3.00	21	14.59	13.8
5	None	C_6H_6	48 hrs.	3.00	3.00	21	16.5	0.6
6	None	C_6H_6, CCl_4[7]	48 hrs.	3.00	3.00	21	12.2	36
7	None	CCl_4	48 hrs.	3.00	3.00	21	14.58	13.9
8	None	CCl_4	48 hrs.	6.08	6.00	21	15.1	10.2
9	None	CCl_4	48 hrs.	1.00	1.00	21	16.0	3.8
10	None	CCl_4	23 hrs.	3.00	3.00	35.0	8.87	87.1
11	EtOH	CCl_4	48 hrs.	3.00	3.00	21	10.90	52.3
12	CCl_4	CCl_4	48 hrs.	3.00	3.00	21	9.31	78.3
13	EtOH, CCl_4	CCl_4	24 hrs.	3.00	3.00	21	12.8	29.7
14	EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	9.44	75.8
15	55° vac./16 hrs.	CCl_4	48 hrs.	3.00	3.00	21	16.54	0.4
16	EtOH, CCl_4; 55° vac./24 hrs.	CCl_4	48 hrs.	3.00	3.00	21	16.56	0.2
17	55° vac./20 hrs.; re-equilibrated	CCl_4	48 hrs.	3.00	3.00	21	13.08	26.9
18	55° vac./16 hrs.; EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	9.56	73.6
19	None	CCl_4	1 hr.	3.00	3.00	62	13.41	23.8
20	None	CCl_4	2.5 hrs.	3.00	3.00	62	8.88	86.9
21	None	CCl_4	5.75 hrs.	3.00	3.00	62	5.47	203.5
22	None	CCl_4	2 hrs.	1.0	1.0	62	14.63	13.5
23	None	CCl_4	5.00 hrs.	3.00	3.00	24.9	16.57	0.2
24	None	CCl_4	5.00 hrs.	3.00	3.00	35.0	16.20	2.5
25	None	CCl_4	5.00 hrs.	3.00	3.00	45.5	12.01	38.2
26	None	CCl_4	5.00 hrs.	3.00	3.00	64.4	5.81	185.7
27	None	CCl_4	40 mins.	0.30	0.50	64.5	16.54	0.4
28	EtOH, CCl_4	CCl_4	48 hrs.	0.50	0.50	62	12.17	36.4
29	EtOH, CCl_4	Et_2O; 1 g. H_2SO_4/mol lactone	48 hrs.	3.00	3.00	21	15.05	10.3

[1] The wools were soaked successively for at least 24 hrs. in each of the solvents indicated. Solvent treatment alone had no effect on the nitrogen analyses. Reagent-grade solvents were used.

[2] Wool was weighed at 21° C, 65% R. H.

[3] Constant to ±1° C or better.

[4] Each value is the mean of 4 or more Kjeldahl analyses on at least 2 separate runs, reproducible to ±0.1%. Analyses are on a moisture-free basis (dried for 40 hrs. *in vacuo* at 70° C).

[5] A domestic, medium-to-fine, soap-and-soda-scoured apparel wool.

[6] Conditioned at 65% R. H., 21° C.

[7] 13 mol % CCl_4.

2. Pretreatment with the solvents alcohol and/or carbon tetrachloride and ether before lactone modification promotes reaction in ether and carbon tetrachloride (experiments 4, 11–14, 38–46); reaction also occurs in chloroform (experiment 47). If the wool is thoroughly oven-dried, no modification takes place in ether or carbon tetrachloride (experiments 15, 16, 37); the reactivity in carbon tetrachloride may be restored by re-equilibration with the atmosphere (experiment 17) or by soaking in "dry" solvents (experiment 18).

3. For the reaction with air-dry wool, reaction is best achieved with a lactone-to-wool ratio greater than unity, although an increase above about 3 is not particularly advantageous (experiments 7, 8, 9, 20, 22, 39, 43, 45).

4. Although no quantitative result is obtainable from the data, a first-order loss of lactone is very approximately followed after the reaction is under way. Experiments 20 and 21, for example, give first-order rate "constants" of 0.17 $hr.^{-1}$ and 0.21 $hr.^{-1}$, calculated from the loss of lactone after the first hour of reaction (experiment 19). This is in accord with attachment of the lactone at specific groups, followed by chain growth at a fixed number of points.

5. The effect of temperature on the reaction is shown in experiments 23–26.

6. The reaction is little affected by the presence of acid (experiments 4, 29, 30). Under these conditions the acid does not polymerize the lactone [3].

7. Vapor application of propiolactone is possible

TABLE II—*Continued*

Expt. No.	Pretreatment[1]	Solvent	Time	Lactone conc. (%)	Lactone-to-wool ratio[2] (g./g.)	Temp.[3] (°C)	Total N[4] (%)	Uptake of propiolactone (%)
30	EtOH, CCl_4	Et_2O; H_2SO_4 only	48 hrs.	0	—	21	16.80	(−1.2)
31	None	Vapor[8]	24 hrs.	—	—	21	16.2	2.5
32	None	Vapor	8 days	—	—	21	13.05	27.2
33	55° vac./16 hrs.	Vapor	9 days	—	—	21	10.46	58.7
34	EtOH, CCl_4; 55° vac./16 hrs.	Vapor	7 days	—	—	21	5.14	223.0
35	EtOH, CCl_4	Vapor	5 days	—	—	21	8.47	96.0
Wool No. 2[9]							16.75	
36	None	Et_2O	1 day	29	15	21	16.43	1.9
37	24 hrs./100°C	Et_2O	1 day	29	15	21	16.47	1.7
38	EtOH, C_6H_6, Et_2O	EtO_2	1 day	29	15	4	15.68	6.8
39	EtOH, C_6H_6, Et_2O	EtO_2	3 days	29	15	4	15.43	8.6
40	EtOH, C_6H_6, Et_2O	Et_2O	1 day	29	15	21	14.92	12.3
41	EtOH, C_6H_6, Et_2O	Et_2O	2 days	29	15	21	14.64	14.4
42	EtOH, C_6H_6, Et_2O	Et_2O	3 days	29	15	21	10.65	57.3
43	EtOH, C_6H_6, Et_2O	Et_2O	3 days	15	7.5	21	11.68	43.4
44	EtOH, C_6H_6, Et_2O	Et_2O	7 days	29	15	21	7.21	132.3
45	EtOH, C_6H_6, Et_2O	Et_2O	2 days	100	ca. 100	21	11.06	51.4
46	EtOH, C_6H_6, Et_2O	Et_2O	15 days	29	15	21	2.71	518.1
47	EtOH, C_6H_6, Et_2O	$CHCl_3$	1 day	16	15	40	10.74	56.0
Wool No. 3[10] *(coarse)*							16.83	
48	EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	15.27	10.5
Wool No. 4[11] *(medium)*							16.75	
49	EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	12.85	30.5
Wool No. 5[12] *(fine)*							16.82	
50	EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	14.01	20.2
Mohair[13]							17.0	
51	EtOH, CCl_4	CCl_4	48 hrs.	3.00	3.00	21	10.32	64.7

[8] Wool was allowed to stand in a desiccator containing propiolactone vapor at about 8 mm. pressure (room temperature).
[9] A New Zealand merino wool which had been scoured with an alkylbenzene sulfonate and soda ash.
[10] A solvent-scoured wool, Columbia ram quarter-blood, 48's–50's.
[11] A solvent-scoured, domestic, medium-blended wool (Columbia, Corriedale, and Targhee), 58's–60's.
[12] A solvent-scoured Rambouillet, 64's–70's.
[13] Shoulder sample from a mature Angora doe; solvent-scoured.

(experiments 31–35). In this case, prior oven-drying does not inhibit the reaction.

8. The rate of reaction varies considerably with the wool used (experiments 14, 48, 49, 50). There is no apparent correlation of rate with fiber fineness. Modification of mohair is also possible (experiment 51).

Mechanism of Propiolactone Modification

A number of techniques have been employed to determine the manner by which propiolactone is bound to wool. First of all, it is evident from microscopic examination that the propiolactone penetrates the fiber. With increasing uptake of the lactone, the diameter of the fiber and its density increase significantly. The surface scale structure is apparently little affected, however, even in the excessively treated fibers. Microscopic cross sections* show that propiolactone penetrates between the spindle cells as a first step.

Also, marked alteration in the x-ray pattern of wool is observed upon propiolactone modification [23]; the first stage of modification appears to involve interaction with the amorphous part; with higher degrees of treatment the crystalline areas are affected and evidence for polymer formation is observed. Complete discussion of these results will be presented in subsequent publications.

A. Amino Acid Assays of Modified Wools

Several chemical aspects of the modification have been investigated. We shall consider first the influence of modification upon the separate amino acids, as determined by microbiological assays of the protein hydrolyzates. It is recognized that the hydrolysis required prior to amino acid determination may sever propiolactone derivatives of the amino acid residues, but in any case where modification causes a decrease in the amount of a specific amino acid the result will be considered as significant indication that this residue is a site of attachment for propiolactone.

The wool used for these studies was a fine-grade, California-grown, Austral-Asian merino wool. It was solvent-scoured successively with benzene, alcohol, ether, methanol, acetone, and water. After being dried at 55°C it was carded several times and manually picked clean. No correction was made for the ash content, which was 0.04%. Modification was achieved by prior soaking with alcohol and carbon tetrachloride, followed by treatment with 3% propiolactone in carbon tetrachloride (lactone-to-wool ratio, 3:1) at 21°C for 2 and 4 days, giving 15.64% and 57.13% propiolactone uptake, respectively. Following treatment, the samples were thoroughly washed with carbon tetrachloride, alcohol, and water. Hydrolysis was carried out with 6*N* HCl for 25 hrs. at 125°C.

TABLE III. MICROBIOLOGICAL ASSAYS FOR AMINO ACIDS OF PROPIOLACTONE-TREATED WOOLS

Amino acid	Original wool (17.08% N) (%)	Wool with 15.64% uptake of propiolactone (14.77% N) (%)	Wool with 57.13% uptake of propiolactone (10.87% N) (%)
Alanine	4.08	3.85	4.05
Arginine	9.20	9.19	9.21
Aspartic acid	6.6	6.7	6.5
Cystine*	13.0	11.7	10.6
Glutamic acid	13.5	13.0	12.0
Glycine	5.41	5.49	5.61
Histidine	1.02	0.35	0.20
Isoleucine	3.69	3.61	3.79
Leucine	7.66	7.78	8.03
Lysine	3.05	2.42	2.20
Methionine	0.50	<0.02	<0.02
Phenylalanine	3.53	3.60	3.65
Proline	6.38	6.70	6.46
Serine	7.59	7.29	6.95
Threonine	6.47	6.14	5.88
Tyrosine	4.29	4.01	4.23
Valine	5.90	5.99	5.96

* Determined by Mecham's modification of Vassel's method [20].

The results are reported in Table III. The percentages given, as grams of amino acid per 100 g. dry-weight of wool, have been corrected, in the cases of the treated wools, to correspond to the original weights of wool before treatment. This was done by multiplying the percentage found by the ratio of the total nitrogen values for the original and treated wool.

It appears that rather extensive reaction of propiolactone takes place with histidine and methionine side-chains; there is also reduction in the number of cystine and lysine residues, and probably interaction with glutamic acid, serine, and threonine groups. It is shown in section *B* (below) in the description of acid-sorption experiments that the number of basic groups in the untreated wool is closely accounted for by the assay values for argi-

* Prepared by Dr. J. I. Hardy, Animal Fiber Division, Bureau of Animal Industry, U. S. Department of Agriculture, Beltsville, Md.

TABLE IV. AMINO-NITROGEN CONTENT OF MODIFIED WOOLS

Wool	Calc. from lysine content* (%)	Van Slyke value* (%)
Untreated (17.08% N)	0.29	0.29
Treated (14.77% N)	0.23	0.19
Treated (10.87% N)	0.21	0.19

* These values have been corrected for the increase in mass accompanying the reaction in order to have them correspond to the original weight of wool before modification.

TABLE V. SORPTION OF HCl BY PROPIOLACTONE-TREATED WOOLS
(pH 1.1; 21°C; MERINO WOOL)

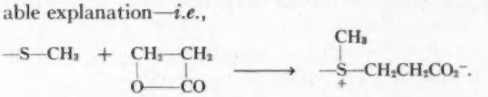
N (%)	Meqs. HCl/g. wool	Meqs. HCl/g. original wool	Amino N* (%)
17.08 (untreated)	0.827	0.827	0.29
14.77	0.518	0.599	0.19
10.87	0.277	0.435	0.19
5.97	0.164	0.469	0.20

* *Cf.* Table IV. These values are corrected for the mass increase accompanying the reaction.

nine, lysine, and histidine. In order to obtain quantitative agreement with acid-sorption results, however, it is necessary that the arginine percentages for the two treated wools be reduced to 7.16% and 4.74%, respectively. This discrepancy might be attributed to instability of the reaction product of the propiolactone and the arginine residue under the hydrolysis conditions employed prior to assay—*i.e.*, the arginine may be regenerated in this process. This may also explain the somewhat unexpected lack of evidence for reaction with aspartic acid and tyrosine.

The lysine assays are in approximate accord with the amino nitrogen percentages, as shown in Table IV. The Van Slyke manometric procedure [27] was used, with a 15-min. reaction period. Analyses are on a moisture-free basis (dried for 40 hrs. at 70°C), and were reproducible to ±0.02.

The reaction with methionine could be explained if this residue were an end-group in the wool protein, but so far there is no evidence for this [22]. The formation of a sulfonium salt is a more probable explanation—*i.e.*,



In this connection we have noted that propiolactone polymerizes fairly readily in the presence of ethyl *n*-butyl sulfide, and it seems likely that the initial step must be of the sort shown above. Possibly, a similar reaction occurs with cystine.

B. Acid Binding of Propiolactone-Modified Wools

The course of reaction indicated by the results of the microbiological assays would require a decrease in number of basic groups in wool by interaction with *beta*-propiolactone. This decrease was confirmed by study of the acid binding of untreated and modified wools; the results indicate that the amount of acid bound by the modified wools is considerably less than that of untreated samples.

The acid binding of wool has been studied extensively [1, 18, 24, 26]. For this work we have used hydrochloric acid at a concentration of about 0.1 *N*, because this gives a maximum uptake for normal wool and also because at this pH the quantity of acid combined is independent of ionic strength [26].

Samples of the merino wool which was used for the assays were conditioned to 63% R.H. in a humidor over saturated ammonium nitrate at 21°C [14]. After standing for 10 to 14 days and having attained a constant weight over a period of several days, 2-g. samples were immersed in 100.00 ml. of 0.1006*N* HCl (pH 1.1) for 11 days. (For one sample, essentially identical values were obtained for 7- and 11-day equilibration; in any event, treatment at 21°C and pH 1 probably causes negligible hydrolysis.) The final acid concentration was determined by titration with standard base to a phenolphthalein end point. The results are given in Table V in terms of milliequivalents of HCl per gram (dry weight) of the original wool. Correction has been made for the moisture taken up by the wool, assuming, as previous workers have done [1, 25, 26], that this is the same as the value for water sorbed from the vapor phase at 100% R.H., and that this sorbed water dissolves no HCl. Moisure sorption data for modified wools are reported in section *F* (below). The use of this correction has little effect on the relative acid-binding values.

The value in Table V for untreated wool is in accord with the results of Steinhardt and Harris [26] and Speakman and Stott [25], which range from 0.80 to 0.84 meqs./g. at pH 1 and 0°C; the values at 25°C are similar [26].

The microbiological assays for lysine, histidine, and arginine (Table III) give, assuming one equiva-

TABLE VI. PROPIOLACTONE TREATMENT OF ACETYLATED AND/OR METHYLATED WOOLS (LACTONE-TO-WOOL RATIO, 3:1; PRIOR SOLVENT "DRYING")

Sample No.	Wool	Time of treatment	Temp. (°C)	Uptake of propiolactone* (%)
1	Control†	48 hrs.	21	15
2	Acetylated‡	48 hrs.	21	17
3	Acetylated‡	6 days	21	46
4	Control†	3 days	21	134
5	Acetylated and Methylated§	3 days	21	110
6	Acetylated and Methylated§	6 hrs.	51	106
7	Control†	6 hrs.	51	47
8	Control†	3 days	21	9
9	Methylated‖	3 days	21	15.5
10	Control†	48 hrs.	25	16
11	Methylated‖	48 hrs.	25	31
12	Control†	6 hrs.	48	61
13	Methylated‖	6 hrs.	48	61

* Calculated from total nitrogen percentages.

† Wool was carried through the same process as acetylated or methylated wools (solvents without acetylating or methylating agent). As noted in the section on Conditions of Treatment, prior solvent treatments are very important in determining the extent of reaction. Hence, for example, the difference between samples 4 and 8.

‡ By the procedure of Blackburn and Phillips [3]. Analyzed, by their method, as 22.2% acetyl; amino nitrogen (Van Slyke method) reduced on treatment from 0.38% to 0.18%. All of the acetyl was not recoverable after propiolactone treatment. Samples 2 and 3, for instance, contained 8.61% and 15.01% acetyl (corrected for mass increase) after propiolactone treatment; the Van Slyke values decreased to 0.12% and 0.11%, respectively.

§ By the procedure of Blackburn and Phillips [3]; amino nitrogen (Van Slyke method) reduced from 0.33% to 0.05%; total nitrogen reduced from 16.69% to 15.19%.

‖ Procedure of Fraenkel-Conrat and Olcott [6] (6 days at room temperature in 0.1*N* methanolic HCl); 3.4% increase in weight.

lent of HCl sorbed per amino acid residue, 0.802 meqs./g. for the untreated wool, in good agreement with the acid-binding value. The treated wools do not give agreement; as discussed in section *A* (above), this is probably due to failure of the assay procedure to detect the modification of arginine.

The acid-binding of the treated wools is in the expected direction; furthermore, the leveling-off in acid binding, noted after the total nitrogen content has fallen to about 11%, is also observed in the amino-nitrogen values. These results indicate that basic groups are involved, but to only a limited extent, in the reaction of wool with propiolactone.

C. Modification of Acetylated and Methylated Wools

The evidence presented above indicates that blocking of amino or carboxyl groups should not inhibit the reaction of wool with *beta*-propiolactone, and this has been found to be the case. Partial blocking of these groups was achieved by acetylation and methylation procedures, and the results of treatment of these "blocked" wools are summarized in Table VI. The wool used for these experiments was a soap-and-soda-scoured domestic 58's to 60's grade.

From the data presented it is seen that neither partial methylation, nor acetylation, nor the combination of the two treatments causes inhibition of the modification by propiolactone. It will, in fact, be noted that a somewhat greater rate of modification may occur with the "blocked" wools.

It is concluded, in accord with the previous results, that the amino and carboxyl groups are not necessary as anchor sites for modification by propiolactone. The greater rates of reaction in the "blocked" wools might be attributed to increased rates of penetration of the fiber caused by the alteration in the structure.

The absence of acid anti-catalysts noted in Table II is further evidence that basic groups are not necessary sites of reaction of wool with propiolactone.

D. Alkali Solubilities of Propiolactone-Treated Wools

One would expect that the introduction of carboxyl groups at the expense of basic groups, as

TABLE VII. ALKALI SOLUBILITIES OF PROPIOLACTONE-TREATED WOOLS

N (%)	Alkali solubility (%)	Alkali solubility, calc. (%)
17.07 (untreated wool)	8.27 ± 0.04	(8.3)
14.77	35.9 ± 0.5	21
10.87	59.8 ± 3.2	42

indicated above, would increase the alkali solubility of the wool. This property of the modified wools has been studied, using the procedure of Harris and Smith [13]. The technique involves measurement of the solubility of wool treated for 1 hr. with 0.1*N* NaOH at 65°C. The same wools were used as described previously for the assay data; the results are shown in Table VII. Each value is the mean of two determinations, with the deviations indicated. The third column gives the alkali solubility to be expected, assuming that the additional weight acquired by the wool is merely a polymer of the lactone and that the polymer is completely dissolved. It was found that under the conditions of the experiment solid polymers of propiolactone dissolved readily, as reported by Gresham *et al.* [8]. The fact that the solubilities are significantly greater than can be accounted for on this basis probably indicates that most of the propiolactone is chemically bound to the wool, thus altering the solubility characteristics of the protein.

E. Acetone Extraction of Propiolactone-Modified Wools

That at least part of the propiolactone polymer is not chemically bound to the wool is shown by extraction of treated wools with hot acetone, a solvent which dissolves propiolactone polymers of molecular weights up to about 900 [8]. Excessively treated wools afforded, on extraction, low-melting solids which were similar in appearance to polymers prepared from propiolactone by low-temperature acid-catalyzed polymerization [8]. Extraction was carried out for several hours with boiling acetone in a well-insulated Soxhlet extractor. Results are given in Table VIII.

Untreated and moderately treated samples 1 and 2 show little or no weight loss on extraction, but further modified samples 3 and 4 are appreciably soluble in acetone. Sample 5, which was prepared by vapor-phase treatment, lost less weight than sample 4, although it was more extensively modified. This may indicate that surface-type polymerization is less likely to occur in vapor modification. X-ray studies [23] of the extracted samples indicate the diffraction pattern typical of propiolactone polymers after the soluble polymer is removed by extraction. Hence, these results also may be interpreted in terms of predominantly an initial reaction with groups attached to the protein followed by polymerization.

TABLE VIII. ACETONE EXTRACTION OF PROPIOLACTONE-MODIFIED WOOLS

Sample No.	Uptake of propiolactone* (%)	Weight loss on extraction* (%)
1	0.0	0.4
2	15.6	0.0
3	57.1	5.4
4	131.7	16.5
5	223.2†	7.4

* Calculated from nitrogen analyses.
† Lactone applied from vapor.

TABLE IX. MOISTURE SORPTION OF PROPIOLACTONE-MODIFIED WOOLS

		63% R.H.		100% R.H.	
N (%)	Amino N* (%)	Adsorption regain (%)	H_2O/N (g./g.)	Adsorption regain (%)	H_2O/N (g./g.)
17.08	0.29	14.7	0.86	36.0	2.1
14.77	0.16	10.8	0.73	27.7	1.9
10.87	0.12	6.6	0.61	21.0	1.9
7.96	0.06	5.32	0.67	20.5	2.6
5.97	0.07	4.21	0.705	—	—

* Van Slyke method [27].

F. Moisture Sorption of Propiolactone-Modified Wools

In connection with the study of acid sorption in section *B* (above), the moisture sorptions of propiolactone-modified wools were investigated. It was found that propiolactone-modified wools have considerably less affinity for water than untreated wool. The data are reported in Table IX.

For the measurements at 63% R.H., 1- to 5-g. samples of the wool described in section *B* were conditioned for from 5 weeks to 3 months in a humidor over saturated ammonium nitrate at 70°F [17]. They did not change in weight over a period of several weeks. Moistures were then determined from the weight loss on drying *in vacuo* for 3 days at 55°C and cooling over P_2O_5. For the data at

100% R.H., samples were conditioned for 2 weeks to constant weight in a humidor containing water at 21°C, dried for 24 hrs. *in vacuo* at 55°C, cooled over P_2O_5, and the weight loss recorded. After drying, the samples were returned to the humidors and the process repeated several times, with reproducible results, using only 5–10 days' time for equilibration.

The data indicate that there is an initial fall in water sorption per gram of total nitrogen, followed by an increase on extended treatment. The initial decrease is in accord with data in the literature (*e.g.*, [21]), which indicate that water absorption is primarily related to the number of specific polar-sorptive groups present, such as lysine. Since part of these are attacked by propiolactone, the lower water sorption on treatment is understandable if it is assumed that the carboxyl or hydroxyl groups which supplant these polar-sorptive groups have a lower water-sorption capacity.

The subsequent increase in water sorption per gram of total nitrogen cannot be attributed to moisture sorption by propiolactone polymer, for it was found that under the conditions of the determination such polymers were not hygroscopic. For example, a polymer prepared by Gresham's procedure [8], melting range 75°–78°C, had a moisture content of 1.32% at 63% R.H. and 70°F.* Possibly the increased fiber size caused by the polymerization makes mechanical occlusion of the water more important on extended treatment—*i.e.*, frees hydrophilic groups that are otherwise unavailable for hydrogen-bonding.

In this connection it may be noted that sorption of water from the liquid phase is also reduced by propiolactone treatment. Soaking of loose wool in water followed by wringing and reweighing indicated that for 60% propiolactone uptake the regain of the treated wool was roughly half that of the untreated samples.

G. *Stress-Strain Behavior of Propiolactone-Modified Wools*

Additional insight into the mechanism of the propiolactone modification of wool is obtained from comparison with the stress-strain behavior of untreated control wools. As will be shown in another paper [19], the effect of propiolactone modification on the mechanical properties of wool is such that the wet fiber is more easily extensible than normal. The wet stress-strain response exhibits lowered yield stress. The effect is analogous to that caused by known hydrogen-bond-breaking agents, and is explicable on the basis that propiolactone serves to wedge apart the constituent chains in the fibers. That decreased bonding of the network chains is the chief factor for increased extensibility, rather than the increased swelling by solvent, is indicated by the observed lowering of moisture sorption accompanying the modification. The bound propiolactone acts, therefore, as a plasticizer for the wool fiber.

* In a recent paper, Katchman and McLaren (*J. Am. Chem. Soc.* **73**, 2124 (1951)) reported low water sorption of polyesters and high sorption of carboxyl groups. These observations and the similar findings by Dole and Faller (*J. Am. Chem. Soc.* **72**, 414 (1950)) are in accord with our moisture-sorption findings, which support our conclusion that polymerization of propiolactone is the predominating reaction in the wool fiber.

Summary

beta-Propiolactone, dissolved in organic solvents or applied as the vapor, reacts with wool to give a product of greatly different chemical and physical properties. The amount of preswelling by solvent treatment is important in determining the extent of modification.

Microscopic evidence indicates a significant increase in diameter upon modification without apparent effect upon the scale structure. The results of microbiological assays, studies of acid sorption and alkali solubility of modified wools, and investigation of the reaction with acetylated and methylated wools indicate that the reaction with wool probably involves initial attachment at histidine, methionine, cystine, and lysine, and possibly glutamic acid, serine, and threonine. This initial reaction is probably followed by an "anchored" polymerization at these sites. There is also some formation of polypropiolactone not chemically bound to the protein, since part of the polymer is extractable with boiling acetone. The modified wools adsorb much less water than untreated wool under the same conditions.

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Part II: Effect on Rate and Degree of Felting *

IN PART I it was shown that *beta*-propiolactone reacts with wool to yield a product having appreciably modified physical and chemical properties. Of these altered characteristics the most significant is the increased tendency of loose wool to felt.

The tendency of wool to felt is one of the unique properties of this fiber. Although this property has been studied extensively [1, 5, 8, 16, 17, 18], the mechanism of felting is rather incompletely understood. Most investigators agree that felting is related to differential friction effect (D.F.E.), but that, in addition, internal friction, characterizing the "rubberiness" of the fiber, is involved.

The effects of chemical treatments of wool upon felting have been studied largely with the goal of rendering wool nonfelting or shrinkproof, and the partial attainment of this objective has been achieved through such procedures as chlorination, polymer impregnation, alkali treatment, and treatment with sulfuryl chloride, enzymes, etc. [8, 16, 17]. On the other hand, apparently little has been found regarding the possibility of facilitating the felting process by means of chemical modification. The approach to this problem has been through variation of the fulling agent and use of carroting procedures, oxidizing agents, etc. These procedures all probably involve either surface effects or operation on the cystine disulfide linkages. The effect of modification of the structure of the protein side-chains on the fulling process has been investigated in the case of benzoylation of wool [9]; this treatment reportedly gives an increased tendency for fabric shrinkage.

Because of the time-consuming, and hence expensive, nature of the commercial felting process, as well as the wide variation in felting tendency among wools, the study of ways of improving the rate and degree of felting of wool becomes important. In this paper we shall consider in detail the effect of propiolactone modification on the felting properties of wool. Laboratory tests, supported by tests on commercial equipment, have indicated that modified wool felts faster and affords felts which, when dry, have a higher degree of hardness, split-resistance, and tensile strength than those made from unmodified wool.

Experimental

Modification of Wool for Felting Studies

Following the details of modification given in Part I, three solution-treated wool batches were prepared from domestic 58's–60's, soap-and-soda-

* Presented, in part, at a meeting of The Fiber Society in Washington, D. C., Sept. 13, 1950.

scoured, apparel wool. The wool was carded twice before use, and drying was effected by successive washing with absolute alcohol and anhydrous carbon tetrachloride. Carbon tetrachloride solutions of the lactone were used for the treatment.

Batch 1.—A sample of wool (1.2 kg.) was soaked for 75 hrs. in 20 gals. of absolute alcohol, wrung dry, immediately immersed in reagent carbon tetrachloride, and left for 12 days. The modification treatment consisted of soaking the wool for 50 hrs. at room temperature (approximately 22°C) in 20 gals. of a 3.0% solution of lactone in reagent carbon tetrachloride (lactone-to-wool ratio, approximately 3.0). The product was squeezed dry, soaked for 6 hrs. in carbon tetrachloride, and then soaked for 3 days in alcohol. The yield, after drying for 24 hrs. in a draft oven at 40°C was 1.71 kg. Two separate portions of the product gave the following analyses (dry basis):

Sample	% N (Kjeldahl)
1	10.1
2	10.8
Control	16.6

The observed decrease in total nitrogen corresponds to an increase in weight due to an uptake of propiolactone by the wool of about 60%, on the dry basis.

Batch 2.—A sample of wool (1.2 kg.) was soaked for 50 hrs. in absolute alcohol, wrung dry, and then immersed for 9 hrs. in reagent carbon tetrachloride. This was followed by 70 hrs. of modification treatment in 22 gals. of 3.3% propiolactone in reagent carbon tetrachloride. The product was squeezed dry, soaked for 4 hrs. in carbon tetrachloride, and then soaked for 60 hrs. in alcohol. The yield, after being dried in the same manner as batch 1, was 1.8 kg. The following results (dry basis) were obtained: treated, 9.8% N; control, 16.7% N. This analysis corresponds to an uptake of propiolactone of about 70%, dry basis.

Batch 3.—Thirty grams of wool were soaked for 3 days in 2 l. of absolute alcohol, squeezed dry, and then immersed for 1 day in 2 l. of reagent carbon tetrachloride. The modification treatment lasted for 24 hrs. in the presence of sufficient 3.0% propiolactone-carbon tetrachloride solution to afford a lactone-to-wool ratio of 3.0. After the excess solvent was expelled, the product was immersed for 4 hrs. in 2 l. of reagent carbon tetrachloride and then for 3 hrs. in absolute alcohol. The yield, after drying overnight in a 55°C draft oven, was 35 g.

TABLE I. BREAKING STRENGTHS OF CONTROL AND BATCH 1 FELT PADS (FULLING TIME, 3.00 MIN.)

Sample	No. of pads	Break strength (lbs.)
Control	15	11 ± 1
Equal weight of treated wool	7	23 ± 6
Equal bulk of treated wool	7	31 ± 6

TABLE II. BREAKING STRENGTHS OF FELT PADS PREPARED ON ABBOTT MACHINE

Fulling time (min.)	Pounds at break		
	Untreated	Batch 3*	Batch 1†
0.50	0 ± 0	—	17 ± 4
1.00	6 ± 4	10.5 ± 0.0	20.5 ± 3.5
2.00	11 ± 3	—	32.5 ± 1.5
3.00	11 ± 1	19 ± 2	33 ± 6
6.00	27 ± 0	—	31.5 ± 4
8.00	31 ± 6	26.5 ± 0.5	—
10.00	20 ± 2	—	55.5 ± 3.5
20.00	27 ± 3	30.5 ± 1	63.5 ± 2.5

* 29% uptake of propiolactone.
† 60% uptake of propiolactone.

The analysis, reported on a dry basis, showed 12.8% N, corresponding to about 29% increase in weight due to uptake of propiolactone.

Laboratory Study of Felting of Propiolactone Wool

The literature contains numerous methods for the quantitative laboratory study of felting (*e.g.*, [5, 6, 7, 14, 16]), including measurement of differential friction, yarn length following milling, area shrinkage of fabrics, compressibility of pads of felted wool, etc. There is considerable question regarding the practical value of such tests because of the multiplicity of factors involved in felting. For the present investigation of rate and degree of felting, a laboratory procedure was adopted which seems to simulate the commercial conditions of felting closely; this procedure is based on the comparative breaking strengths of pads of control and modified wools prepared on an Abbott felting machine (Abbott Machine Co., Wilton, N. H.). The degree of felting, as distinguished by the compactness and hardness of the felt pad, is correlated with the breaking strength of the pad; moreover, as will be shown, the observed large differences between control and propiolactone-modified wools are in accord with results of tests on felts prepared from these wools on commercial machinery. The procedure adopted for preparation of felts on this machine was as follows:

One-and-one-half-gram samples were carded and

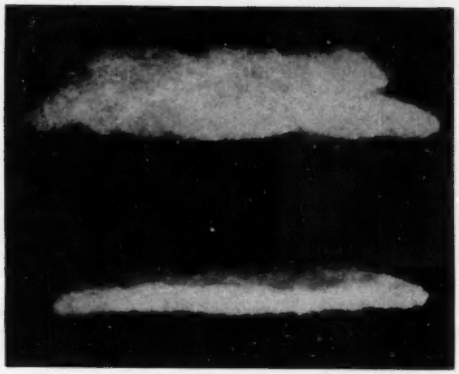

FIG. 1. *Cross-sections of Abbott-machine pads; fulled for 2.0 min.* Above—*Untreated domestic medium wool.* Below—*Batch 1 wool (60% propiolactone uptake).*

placed in the machine by a standard procedure, with 4° Tw. (approximately 0.3*M*) sulfuric acid used as fulling agent to correspond with that used in commercial fulling [19]. Two ml. of the acid was added before introduction of the wool, and 2 ml. was spread on top of the pad. The 5-lb. weight was placed on the wool, and the rapid circular rubbing motion begun. After fulling for a given period, the circular pads were water-washed, dried overnight at 55°C, and conditioned for 24 hrs. at 65% R.H. and 21°C before testing. The pads were then folded double and the breaking strengths measured in the Scott Tester, Model J2, with a 1-in. jaw separation. It is thought that this large jaw separation decreased the likelihood that fiber strength would be a factor in the result obtained.

The same initial quantity of wool was used in tests on the treated wool; the sizes of the correspondingly larger samples of treated wools were calculated from the nitrogen analyses. Separate tests on samples compared on an equal-weight, rather than an equal-bulk, basis gave similar relative values, as shown in Table I for the control and batch 1 (60% propiolactone uptake) wools. Breaking strengths are given for pads compared on an equal-bulk and an equal-weight basis.

Despite the rather poor precision, as shown by the indicated mean deviations, the results indicate that the effect of propiolactone on felting is real and is not attributable merely to a weight increase. Since the equal-bulk pads were easier to prepare on the machine, this technique was employed for all subsequent work.

The difference in degree of felting is visually apparent and is illustrated in Figure 1, which shows cross sections of batch 1 (60% propiolactone uptake) and control pads resulting from 2 min. of fulling in the Abbott machine. Table II summarizes the breaking strength at various fulling times for the untreated wool and batch 1 (60% propiolactone uptake) and batch 3 (29% propiolactone uptake). Two to five pads were run at each fulling time, and the mean deviations of breaking-strength values are tabulated. The reproducibility of the results was only fair but, as shown in Figure 2, the difference between untreated and modified pads (batch 1) was appreciably greater than the limits of precision of the experiment. It will be noted that the final felt strength was greater for batch 1 (60% weight uptake) than for the control or batch 3 (29% weight uptake). This dependence of felt strength on extent of reaction is

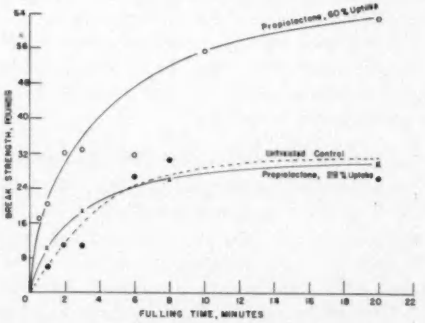

FIG. 2. *Breaking strengths of Abbott-machine pads at various fulling times.*

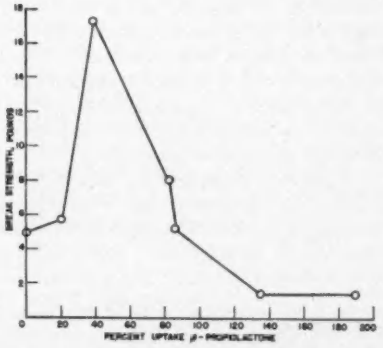

FIG. 3. *Breaking strengths of Abbott-machine pads as a function of propiolactone uptake.*

shown in Figure 3, which gives felt strength after 3 min. of acid fulling as a function of the percentage of uptake of propiolactone. The latter results are not directly comparable with Figure 2, because the data of Figure 3 are for a solvent-scoured, domestic, fine wool.

It is possible to conclude from these two graphs that there is an optimum uptake of propiolactone as far as felting is concerned; this optimum occurs at about 40%–60% propiolactone uptake. It is also apparent that the rate as well as the degree of felting is enhanced by this modification.

Felting of Propiolactone Wool on Commercial Equipment

The ultimate practical index of felting is direct evaluation of felts prepared by standard commercial equipment. We have, accordingly, compared the felting properties of control and propiolactone-modified wools subjected to the felting action of industrial machinery.*

Two steps are employed in preparing commercial felts. The initial "hardening" step, which consists of application of heat and moisture (steam) together with pressure, is followed by the "fulling" procedure, in which the hardened material is pounded with wooden hammers for extended periods of time in the presence of a fulling agent. The fulling agent is usually water or soap or, for the hardest felts, strong sulfuric acid.

In carrying out the initial test runs,† equal bulk portions of batches 1 and 2 and of the control were employed—that is, 100 parts of control to 160 parts of batch 1 and 170 parts of batch 2. The three were initially saturated with steam and pressed, with a rubbing motion, under steel plates for the conventional hardening procedure; they were then saturated with 2.5% sulfuric acid, fulled for 4.5 hrs., rinsed thoroughly, and oven-dried. The modified samples were $\frac{1}{2}$ in. thick, compared with $\frac{3}{8}$ in. for the control felt. It was noted that the modified wool gave felts which were very hard when dry, but quite soft and pliable when wet.

Of the laboratory evaluation tests of felts used industrially, the best correlation with wear-resistance is apparently obtained with the split-resistance test; the results of split tests performed on the products according to A.S.T.M. specifications [3] on a Scott Tester are given in Table III, together with hardness values as determined with a durometer (U. S. Rubber Co., Rex Model A).

TABLE III. SPLIT-RESISTANCE AND DUROMETER HARDNESS VALUES OF *beta*-PROPIOLACTONE-MODIFIED WOOLS

Sample	Uptake of propiolactone (%)	Split-resistance (lbs.)	Hardness
Control	0	91	55
Batch 1	60	130	65
Batch 2	70	136	65

TABLE IV. SHRINKAGE DURING FULLING OPERATION OF 50% (BY BULK) BLENDS WITH A TEXAS WOOL

Fulling	Control (%) Length	Control (%) Width	Batch 1 (%) Length	Batch 1 (%) Width
30 min. in soap	20.4	6.8	22.8	24.3
1 hr. in soap	26.4	16	32	27.3
1 hr. in soap, then 30 min. in acid	34.1	19	39.5	30.4

TABLE V. FELT DENSITY AND HARDNESS

Sample	Uptake of propiolactone (%)	Density (g./ml.)	Durometer hardness
Control	0	0.242	30
Batch 1	60	0.313	45
Batch 2	70	0.365	50

Since the split-resistance values are reproducible to within 1 or 2 lbs., the difference is definitely significant.

In a second test run,‡ the effect of shrinkage was determined; in the felt industry this is used as a measure of the amount of felting. In this case, a 50-50 blend (bulk basis) of the control and batch 1 wools with a Texas wool, which was in use as a commercial felt stock, was employed. The data of Table IV were obtained for these samples.

The increased shrinkage resulting from the modification is apparent. Also, the altered handle and greater firmness of the treated samples indicate enhanced felting properties.

Felts Prepared on a Laboratory-Model Hammer Mill

Propiolactone-treated wool felts have been prepared** on the Furness-model hammer mill [10]. Samples of equal bulk were fulled 2,400 strokes with soap solution as fulling agent; the felts were washed, dried, and then fulled another 2,400 strokes with 2.5% sulfuric acid. A markedly greater hard-

* Through facilities made available by the Standard Felt Company, Alhambra, Calif., and the Felters Company, Millbury, Mass.

† At the plant of the Standard Felt Company, Alhambra, Calif.

‡ By the Felters Company, Millbury, Mass.

** Through the courtesy of the Standard Felt Company.

TABLE VI. SHRINKAGE OF *beta*-PROPIOLACTONE-MODIFIED FLANNEL CLOTH

Sample No.	Treatment	Propiolactone uptake (%)	Area shrinkage (%)
1	None	0	14.4
2	None	0	19.9
3	None	0	14.5
		mean	16 ± 2
4		33.9	34.4
4	3% propiolactone; 48 hrs./room temp.	34.2	31.6
6		41.9	41.1
7		0	13.8
8	Solvents only (controls on samples 4–6)	0	10.1
9		0	12.1
		mean	12 ± 1
10		28.6*	26.1
11	Conditioned at pH 8.8, then treated the same as samples 4–6	30.1	26.7
12		31.1	29.1
13	3% propiolactone; 97 hrs./room temp.	79.8	19.9
14		94.3	22.8
15	Same as for samples 13 and 14, then extracted 17 hrs. with boiling acetone	84.6 (66 after acetone extraction)	40.1

* It was thought that pretreatment with basic buffer might make the wool more susceptible to reaction by freeing the basic groups, but, as shown in runs 4–6 and 10–12, this had no significant effect on the result.

On the basis of weight after pH 8.8 treatment. The buffering caused a weight loss of 0.4%, 0.1%, and 0.2%, respectively, for these samples.

ness is observed for the propiolactone-treated wool samples than for the control; this is reflected in the higher density values reported in Table V. These results were obtained after drying the cylinders at 100°C for several hours; the durometer hardness values were determined independently.

Fabric Treatment: Effect of Propiolactone Modification on the Shrinkage of Wool Flannel Cloth

Direct propiolactone modification of flannel cloth also affects the felting ("fulling") as measured by shrinkage tests. For this study, 3-in.-square pieces of an unfinished wool flannel were conditioned at 65% R.H. (21°C), weighed, and subjected to propiolactone modification in the same way as loose wool. After reconditioning and weighing, the cloths were allowed to relax for 1.5 hrs. in 0.5% aqueous sodium oleate and were then hand-milled for 5 min. in this solution at 26°C (modification of procedure of Alexander *et al.* [2]). Following thorough water-washing and reconditioning, the cloths were pressed between glass plates and the areas remeasured. There was less than 10% weight loss on milling. The results are given in Table VI.

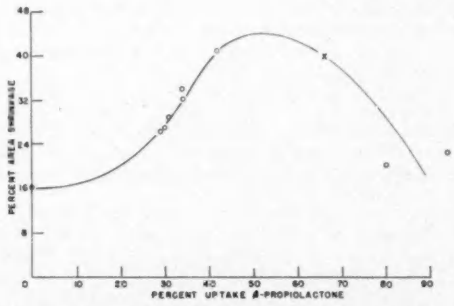

FIG. 4. *Shrinkage of wool flannel cloth as a function of propiolactone uptake.*

Samples 1–3 received no treatment; samples 4–6 were soaked in absolute alcohol for 24 hrs. and in reagent carbon tetrachloride for 24 hrs., and were then treated with 3.0% propiolactone in carbon tetrachloride (lactone-to-wool ratio, 3:1) for 48 hrs. at room temperature. Samples 7–9 were solvent-treated only (controls on samples 4–6); samples 10–12 were pretreated with a pH 8.8 sodium borate buffer, rinsed with water, dried at 55°C, and then treated as were samples 4–6. Samples 13–15 were treated for 97 hrs. at room temperature; sample 15 was then further extracted for 17 hrs. with boiling acetone.

The results of these experiments are given graphically in Figure 4. Again there is a maximum in the shrinkage-extent of reaction curve at a point similar to that of Figure 3—*i.e.*, at about 40%–60% uptake. Excessively treated samples showed a shrink-resistance that compared with moderately treated patches, and it was observed qualitatively that treatment at elevated temperatures or for longer periods of time than for samples 13–15 gave fabrics which were quite boardy and which were unshrinkable by the hand-milling procedure used here.

The return of felting power of excessively treated patches on extraction with hot acetone is shown in sample 15 (indicated by an x in Figure 4). The original uptake of 85% after the 97-hr. treatment was reduced to 66% by acetone extraction, and this sample shrank with markedly greater ease than did the other 97 samples. This probably indicates that these extensively treated samples contain large quantities of polymer deposited on the surface of the fiber, and hence exhibit the well-known shrink-resistance imparted by such treatments, since this solvent dissolves propiolactone polymers [11].

Conclusions

It was shown in Part I that *beta*-propiolactone largely reacts with wool *in situ* by an "anchored" polymerization on various reactive amino acid side-chain groups. In Part II the effect of this modification has been described on the rate and degree of felting of loose wool. It was shown that felts prepared from propiolactone-modified wool have, when dry, a high degree of hardness, split-resistance, and tensile strength. The wet felts, however, are softer and more pliable than untreated wool felts. The influence of propiolactone treatment on felting reaches a maximum at 40%–60% by weight uptake of propiolactone. Similar effects of propiolactone modification are observed in the milling shrinkage of woolen fabrics, in which case there is also a maximal effect at 40%–60% uptake. Excessively treated samples may have their felting power restored by extraction of the excess propiolactone polymer with hot acetone.

In a subsequent paper we shall deal with the effect of this treatment on the mechanical properties of wool, including the effect on surface friction, and shall attempt to derive a plausible explanation for the effects of propiolactone modification on felting.

The finding of an optimum degree of felting so far as propiolactone uptake is concerned indicates at least two opposing factors in the felting process. Both elastic properties and the differential friction are important in felting, as has been shown by several workers [4, 12, 13, 14]. It will be shown in the next paper of this series that there is a small but continuous decrease in differential friction with propiolactone uptake, with a concomitant increase in elasticity or "rubberiness." It appears that the optimum degree of felting is explained by the opposition of these two factors.

Acknowledgments

The authors are indebted to the Standard Felt Company, Alhambra, Calif., and to the Felters Company, Millbury, Mass., for permission to publish the results of tests carried out in their plants. The nitrogen analyses were carried out by Mrs. Marian Long of this Laboratory.

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The Relationship Between the Structural Geometry of a Textile Fabric and Its Physical Properties

Part III: Textile Geometry and Abrasion-Resistance*

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Abstract

This paper examines the relationship of structural geometry to the abrasion-resistance of textile fabrics. It is pointed out that the durability of a fabric can be significantly altered by modifying its structural design, without change in the fiber used in its manufacture. Earlier textile studies and heretofore unpublished Army test reports provide illustrations of the relationship between fabric geometry and durability. On the basis of this material, it is believed that lower rates of attrition can best be obtained by increasing the geometric area of contact between fabric and abradant. At the same time, fabric compliance and yarn mobility must be preserved at points of contact between the two rubbing surfaces. Thicker fabrics possessing minimum rates of attrition, consistent with other cloth requirements, will provide optimum durability for fatigue garments.

Abrasive Pressure and Textile Geometry

The nature of metallic wear and the mechanism of textile fabric abrasion are similar in that the rate of destruction of both materials increases with higher normal loads between abradant and test specimen. This similarity may arise from the same or different causes, depending upon the nature of the rubbing. When the abradant has a rough surface and is significantly harder than the metal or textile sample, increased rubbing pressures will cause the sharp protuberances of the abradant to penetrate more deeply into the test specimen, and in this manner the higher abrading load will increase the plowing damage. When the protuberances of the abradant are large and sharp, the abrasion mechanism takes on the aspects of surface cutting. On the other hand, when the rubbing surface is relatively smooth, wear may take place through the mechanism of successive local adhesions and adhesion ruptures between protuberances of the two rubbing surfaces. This type of damage, termed "direct frictional wear," is also dependent upon normal loads between rubbing surfaces. This dependence is due to the fact that higher intersurface loads demand larger areas of true contact between the two bodies, and thus lead to increased total damage. Briefly, in the former instance higher loads cause deeper damage over the same areas, while in the latter case they result in a greater area of damage of the same depth.

Both of these mechanisms have been discussed in Part II of this series (July, 1951, TEXTILE RESEARCH JOURNAL) and they can be observed in the service life of both metals and fabrics. In the case of machinery metals, the discussion of wear is usually limited to the adhesion mechanism, as studied by Bowden and Tabor [2]. In the case of textile materials, however, the range of rubbing surfaces encountered during the service life of the end item is such that both frictional and plowing or cutting (as well as snagging) damage must be considered. In Part II it was also pointed out that frictional adhesion at the cloth surface may result in secondary damage to the fabric which far exceeds the direct effects of frictional wear. This indirect damage is caused by transmittal of frictional forces along the length of the surface fibers, and is evidenced in tensile or bending fatigue of the fiber, or in its removal from the yarn structure.

It is clear that one way of cutting down the wear between rubbing surfaces is to reduce the normal loads between them. However, when intersurface

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Parts I and II appeared in the November, 1948, and July, 1951, issues of TEXTILE RESEARCH JOURNAL, respectively.

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loads are fixed, the designer of durable materials must resort to other methods of reducing wear. In the case of metal, he will smooth and polish both rubbing surfaces and then add a lubricant (with proper bearing design) so as to support the load by means of hydrodynamic pressures rather than by metal-to-metal contact. The smoothing of the bearing surfaces is not intended to increase the area of contact between the surfaces and thus reduce local pressures, but is principally a precaution against gouging by rough spots on either surface. Actually, it has been shown that the true area of contact between two metal bodies (of given hardness), which may be of the order of one-thousandth the apparent or geometric area of contact, is dependent only upon the normal loads between the surfaces. This dependence arises from the fact that the contact points comprising the true area are generally deformed plastically. The bulk rigidity of the metal is so high that the local plastic deformation takes place and the intersurface load is supported by a constant flow pressure over a very small area *before* a large number of points can come into contact.

Burwell [3] pointed out that the bulk flexibility of visco-elastic materials permits numerous protuberances to come into contact before the load between surfaces is completely supported, and this is accompanied by a load reduction at each such contact point. As a result, the proportion of points undergoing plastic deformation will be considerably reduced. The geometric area of contact of individual fibers has been studied by Finch [12], and has been shown to depend upon the normal load at the point of contact, the principal curvatures of the fiber, the contour of the fiber cross section, and the fiber bulk modulus. With fabric structures, bulk modulus is a major factor influencing contact area under a given load. Actually, the apparent bulk modulus of the fabric as affected by the compressibility of its backing support during use must be taken into consideration. A low apparent bulk modulus, or high over-all flexibility, serves to bring as many yarn crowns in geometrical contact with the abrasive surface as is consistent with the fabric structure. The more numerous the crowns in contact and the more area per crown or per projecting yarn float, the less will be the local load at a fiber point. As local load is reduced, the true area of contact at each point is also reduced, and the abradant protuberance will descend into the yarn structure to a lesser degree. As a result, there will be less frictional wear at the local point of contact; less local frictional-resistance to develop axial components of fiber stress; reduced surface cutting of the fibers; and less fiber plucking, slippage, and tensile fatigue. It should be noted that high bulk flexibility of a textile fabric tends to amplify the *total* frictional-resistance observed when a foreign body is rubbed across the cloth because of the increase in total contact area, even though the frictional-resistance at each local point of contact may be reduced. The number of local contact points between fabric and abradant is affected by several geometric factors, each of which is discussed separately below.

Textile Structure and Local Pressures

Threads per Inch

When all other factors are held constant, the abrasion-resistance of warp-flush fabrics is improved by increasing the number of warp crowns per square inch of fabric, thus reducing the normal load per warp crown [27, 29, 30, 47, 49]. This same trend is observed in fabrics varying in weave and yarn diameters, as is indicated in the work of Tait [52] (summarized in Figures 1 and 2). Combat-course tests [41, 53, 59] have likewise shown the effect of warp threads per inch on the durability of a herringbone-twill cotton work garment. In Table I it is seen that a fabric with actual textures of 88 × 59 t.p.i. wore better than one with 77 × 59 t.p.i.; that 89 × 49 fabric wore better than 76 × 48; that 88 × 59 wore better than 89 × 49; that 77 × 59 wore better than 76 × 48. On the other hand, the 82 × 54 fabric wore more poorly than the 77 × 59, but better than the 76 × 48.

While several of the wear-score differences cited above lack precise statistical significance, there is sufficient evidence in the data of Table I and of Figures 1 and 2 to support the following general conclusions: In constructing twill or sateen fabrics with warp yarns exposed at the surface of wear: (1) increased warp textures (at constant pickage) will furnish greater durability; (2) increased filling textures (with a constant number of ends) result in increased fabric cohesion and greater fabric durability.

There are, of course, certain limitations to these conclusions which must be kept in mind in the design of more durable fabrics. If changes in warp crowns are to have an effect on cloth durability,

TABLE I. LABORATORY DATA, CAMP LEE SERIES*

	Group I—Nylon			*Group II—Weave*					*Group IV—Texture (nominal)*					*Group V—Yarn Count*				Standard
	0%N	23%N	50%N	HBT	HBT, M	Plain	Oxford	Sateen	84× 55	84× 45	78× 50	72× 55	72× 45	10× 8	10× 12	16× 8	16× 12	HBT
Fabric No.→	111	114	117	100	103	104	107	112	24	28	31	34	38	15	17	54	56	
Texture (threads/in., actual)																		
Warp	84.1	84.6	84.0	81.3	82.1	81.5	84.9	85.5	88.2	89.1	81.8	76.9	76.1	75.6	76.8	75.6	79.6	76
Filling	62.8	65.3	65.1	53.7	54.9	52.4	53.7	60.6	59.4	49.0	54.3	58.5	47.7	57.0	59.5	59.9	60.9	46
Weight (oz./sq.yd.)	10.2	10.6	10.0	9.9	10.1	9.2	9.7	10.5	10.5	9.7	9.8	10.2	8.7	12.2	10.4	9.8	8.5	8.9
Breaking load (lb.)																		
Strip, Warp	127	124	125	116	116	103	126	101	120	109	112	104	114	118	131	96	97	127
Filling	106	111	108	112	102	121	128	83	116	87	99	111	89	144	97	149	90	87
Grab, Warp	154	150	149	150	148	148	156	152	180	171	156	146	142	199	191	126	115	140
Filling	136	144	122	118	121	140	147	132	157	104	126	146	104	203	113	190	104	146
Elongation, Grab (%)																		
Warp	22.3	24.7	23.8	30.5	31.4	27.2	27.3	25.2	32.2	31.5	34.9	27.0	25.2	32.2	37.3	29.7	26.3	17.7
Filling	24.8	26.5	26.9	20.8	22.6	18.2	23.5	27.4	19.7	18.1	21.4	24.4	20.0	22.5	20.1	24.4	25.3	21.7
Tearing strength (lb.)																		
Tongue, Warp	10.7	10.9	9.3	6.4	6.0	4.5	7.4	10.4	6.3	7.7	6.6	5.9	7.8	7.1	7.6	4.2	4.8	3.8
Filling	7.7	8.1	10.7	4.8	4.9	4.1	5.2	8.4	4.8	5.5	5.6	6.2	5.8	7.1	4.3	7.6	5.2	4.9
Elmendorf, Warp	10.9	11.7	11.5	7.9	7.9	5.5	7.9	12.3	7.1	8.0	7.6	6.7	8.6	7.7	8.2	5.7	6.0	5.9
Filling	12.0	9.4	12.6	6.8	6.2	6.3	6.5	9.2	7.6	6.4	8.4	7.7	9.2	8.7	6.1	10.2	7.7	7.5
Bursting strength																		
Mullen (p.s.i.)	345	311	340	283	284	287	289	348	298	266	282	314	256	402	267	318	260	315
Ball (lb.)	249	264	271	219	175	213	199	237	227	177	263	226	208	302	177	210	219	178
Stiffness (0.001 lb.)																		
Warp	3.1	3.5	4.1	4.4	4.9	3.7	3.5	4.7	10.6	5.7	4.3	6.1	3.6	10.2	8.1	4.3	3.2	3.8
Filling	3.6	3.7	2.1	3.1	4.4	4.4	2.6	2.7	6.5	2.9	3.5	3.8	2.2	7.9	4.7	4.4	2.5	3.6
Thickness (0.001 in., 3.63 p.s.i.)	26.4	27.4	26.5	23.3	23.6	19.5	20.6	29.1	22.6	24.8	23.6	22.4	21.6	25.6	23.3	22.9	20.7	19.5
Camp Lee wear score																		
9th cycle, trousers	8.3	4.9	5.0	33.2	26.1	40.2	29.6	14.5	51.3	56.0	61.2	54.4	67.3	20.8	16.0	29.1	31.3	
Standard control HBT wear score	18.0			40.3					47.4					23.0				

* It will be noted that the wear score of the standard HBT control fabric varies from test run to test run on the combat course, as summarized in Table I. While caution was used in applying techniques of experimental design and statistical interpretation to insure the validity of data from single test runs, there were certain conditions which could not be controlled from run to run. For example, the men assigned as test subjects were changed between runs, and the over-all weather conditions also changed. Considerable time was spent in determining to what extent fabric ranking would vary from run to run. After a careful procedure was inaugurated for screening maverick test subjects prior to each run, it was found that the significant ranking of fabrics was unchanged from run to run, and this enabled the investigator to subsequently use the control results as a weighting factor to compare fabrics among groups (corresponding to runs) as well as within groups.

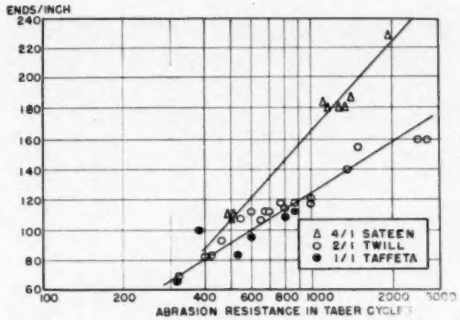

FIG. 1. *Effect of weave on the abrasion-resistance of rayon linings. Fabrics were made of 150-den., 40-filament yarn, warp and filling. Fabrics were viscose or viscose-acetate combinations.* (*Source, Tait* [52].)

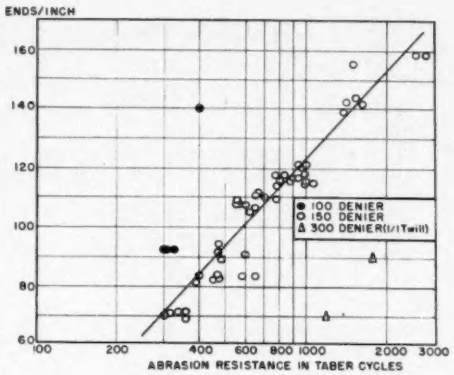

FIG. 2. *Effect of warp yarn count on the abrasion-resistance of viscose rayon linings. Fabrics were 2/1 twill, except one indicated as 1/1 twill.* (*Source, Tait* [52].)

the abraded surface must in all cases be the warp-flush side of the cloth. The greater number of warp crowns per square inch of fabric surface must not be obtained by increasing the warp texture to the point of jamming the warp threads and markedly reducing the flexibility of the fabric structure. Likewise, the filling texture should not be excessive nor the warp float so short that the warp crowns become rigid knuckles incapable of absorbing abrasive energy without early rupture of surface fibers.

Structural changes in textile fabrics often occur in use. The effect of laundering on fabric geometry is one of the most pronounced factors in this connection. Shrinkage serves to increase the number of threads per inch and thus to reduce the wear rate in subsequent rubbing [27]. It follows that laboratory abrasion tests should be conducted on the fabric in the state which it will maintain over the major portion of its service life.

The importance of cohesion as applied to fiber, yarn, and fabric structures has been stressed by investigators of fabric wear-resistance [33, 51]. Cohesion may be obtained in the yarn form by resorting to higher twists, or in the fabric form through use of closer weaves and higher textures. It has been considered desirable to use the latter means of securing cohesion because it permits use of lower yarn twist, which leads to yarn flattening, presentation of greater surface, and reduction of local loads [29].

The abrasion of textile fabrics is so complex a mechanism that the effect of local crown loads on durability is often masked by interactions with other factors. A large part of this complexity is eliminated when the cloth specimen is constructed of monofilament yarns. A single row of vinylidene monofilament crowns rubbed with emery paper shows (Figure 3) the effect of a reduction in crown pressure on depth of cut. Here the total load on the abradant was held constant and the number of crowns supporting the load was varied.

Although many elastic solids give evidence of a straight-line relationship between load and abrasion damage [15], the yarn crowns of Figure 3 do not. One reason for this is the change in crown-abradant contact area which occurs as the monofilament is worn down. The yarn crown in a plain weave resembles a torus, such as is pictured in Figure 4. If sections of this torus are sliced off perpendicular to the z-axis, the area of the exposed surface will vary in a nonlinear fashion. The relationship be-

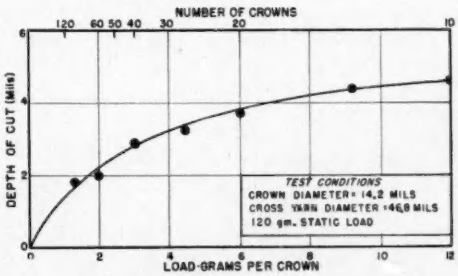

FIG. 3. *Abrasion-resistance of vinylidene monofilaments.*

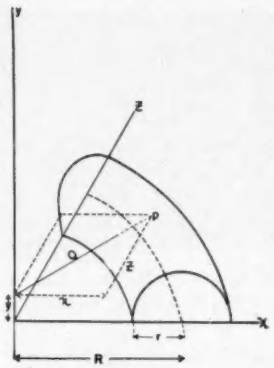

FIG. 4. *Three-dimensional view of torus section formed by crown.*

tween these sectional areas and the depth of cut and torus dimensions has been determined by mechanical integration and is pictured in Figures 5 and 6 for tori with varying inner and outer radii.

By using these curves, one can easily calculate the local bearing surfaces in a plain-weave textile fabric as its thickness is reduced in abrasion. This is, of course, the most elementary case, corresponding to the type of monofilament fabric used for seat covers in railway coaches. In ordinary spun fabrics, where the fibers are not retained in a matrix of starch or other coating material, the surface fibers spring up in a fuzz after abrasive rupture and the yarn structure is radically altered [1, 4]. In addition, the contact areas calculated for the torus do not take into account the effect of compressive changes in the form of the torus itself resulting from normal loads. It suffices to say that in textile materials the contact area will increase as a consequence of wear, but only in the case of monofilament materials can this increase be predicted. It may be expected that the wear rate under constant conditions of abrasion will fall off as the contact area between fabric and abradant increases. This effect is demonstrated in abrasion tests on vinylidene yarn (Figures 7 and 8).

Figure 7a shows the reduction in monofilament thickness at the point of abrasion as the number of rubs increases. These tests were conducted on the apparatus described by Stoll [51]. Several outer yarns of varying diameter were used, each being wrapped around an inner cross yarn (actually a steel wire) of 46.8 mils diameter and subjected to a load of 7.5 g. per outer yarn crown during abrasion with emery paper. The results of a similar test carried out with a reduced load and an increased cross-yarn diameter are shown in Figure 7b. Figures 7a and 7b illustrate the falling-off of the rate of abrasion as the depth of cut increases. This change in slope corresponds to the increase of geometric area of contact shown in Figures 5 and 6. The maximum torus sections plotted in Figures 5 and 6 are seen to occur at a point where approximately three-fourths of the crown yarn has been removed. Since yarn rupture takes place at or before this depth of cut, there is no tendency for the abrasion rate of monofilament crowns to increase in the final stages of the test.

Yarn Diameters

The association of greater wear life with increased thickness of a given material has been reported many times, and implies a direct relationship between the decrease in thickness and the number of

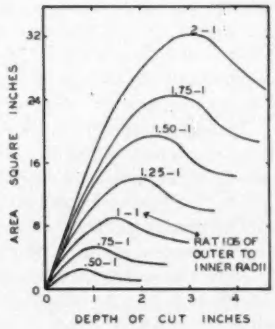

FIG. 5. *Area of torus sections (inner radius = 1 in.).*

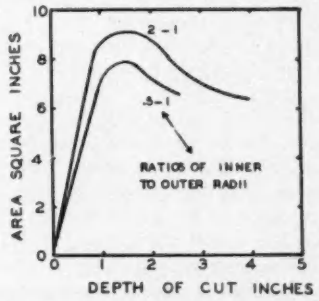

FIG. 6. *Area of torus sections (outer radius = 1 in.).*

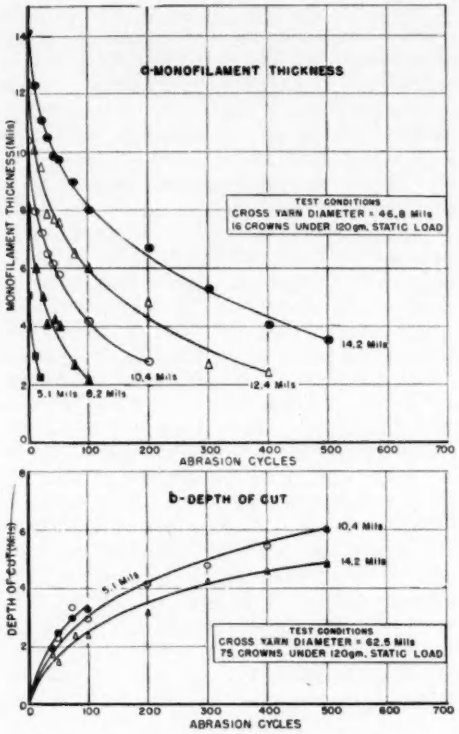

FIG. 7. *Effect of yarn-crown diameter on abrasion-resistance of vinylidene monofilaments.*

rubs in an abrasion machine [15, 43]. Increased fabric thickness and larger yarn diameters are generally related and provide marked improvement in the abrasion-resistance of textile structures. However, the relationship between yarn diameters and fabric thickness is not a simple one. For a given set of balanced yarns, fabric thickness can be varied from the sum of the yarn diameters to $\frac{3}{4}$ of the sum simply by controlling crimp. The abrasion-resistance of the fabric during this change will vary significantly, but by no means proportionately to the change in thickness, indicating that once the surface yarns have been severely abraded, the remaining thickness of the specimen does little more to prolong the life of the fabric [27]. In other words, abrasion-resistance is related to the thickness or diameter of that element of the textile structure which is exposed at the rubbing surface.

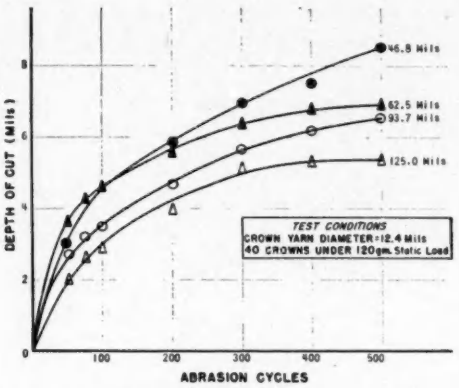

FIG. 8. *Effect of cross-yarn diameter on abrasion-resistance of vinylidene monofilaments.*

Both yarn [18, 56] and fabric abrasion studies [48, 52] have indicated the effect of the diameter of exposed yarns on the abrasion life of textile materials. Tait's detailed data, plotted in Figures 1 and 2, show significant increases in the abrasion life of lining fabrics as heavier yarns are used. Studies of cotton fatigue fabrics [1, 42, 60] have shown significantly longer combat-course life of cotton fabrics with lower warp yarn counts (*i.e.*, heavier warp yarns) since this set of yarns is subjected to the most severe wear in the herringbone-twill structure (see Table I). Corresponding results are reported in laboratory abrasion tests.

When the effect of yarn diameter was evaluated on vinylidene monofilaments, the data plotted in Figure 7a were obtained. The cycles corresponding to the end-point of other types of yarn abrasion tests are represented by the lowest recording on each of the curves for the varied-diameter monofils. These tests were conducted with a 120-g. load on 16 crowns, wound and abraded as indicated above [51]. In a second experiment, the abrasive load was reduced (by increasing the number of crowns) so as to increase the sensitivity of the abrasion test and permit study of the rates of wear on the monofilaments. Data of the second test are plotted in Figure 7b, and represent the depth of cut *vs.* abrasion cycles, rather than monofil thickness *vs.* abrasion cycles. Here the influence of yarn diameter on the rate of wear is clearly indicated, resulting from differences in sectional areas (Figure 5) and therefore in local pressures at points of contact.

FIG. 9. *Surface contact of a cotton sateen under pressure (8.2 lbs. exerted with a hard backing against a sample 1.0 in. by 0.5 in.). Differences in compression due to uneven yarns are indicated.*

Other experiments were conducted using a constant (12.4 mils) diameter crown yarn and modifying the radius of curvature of the bent crown (corresponding to the radius of the cross yarn, or $R-r$ in Figure 4). Here, again, differences in sectional areas of contact may be expected from the yarn geometry. This is seen in Figure 6, in which areas of the torus sections are plotted against depth of cut for constant-radius crown yarns, but with varying cross-yarn radius. The results of the abrasion tests with varying cross-yarn diameters are plotted in Figure 8. Again the influence of sectional areas on rate of abrasion is demonstrated, this time on crown yarns of constant diameter.

It should be emphasized that the larger diameters of the abrasion-bearing yarns must be accompanied by yarn uniformity if increased wear life is desired. Nonuniform heavy yarns actually serve as focal points in fabric degradation because of the high pressure concentrations which occur at their crowns. The irregular compression pattern resulting from nonuniform yarns is clearly indicated in Figure 9, which pictures the contact area of a cotton sateen pressed against a piece of ground glass under a load of 16.4 lbs. per sq. in. [24]. Several heavy filling yarns (shown in the vertical direction) protrude above the nominal surface of the fabric and are therefore subject to higher pressures than the other yarns. These occasionally heavier picks also cause the lighter warp yarns (horizontal) crossing them to rise to the surface and be subject to abrasive damage.

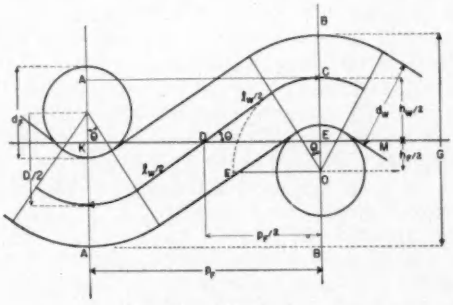

FIG. 10. *Crimp diagram.*

Crimp Distribution

Crimp distribution determines the relative vertical displacement of each set of yarns above and below the plane of the fabric. As defined in studies of cloth geometry [32, 34], true crimp, c, is the ratio of the differences between the axis length of a yarn, l, and its horizontal projection, p, to the horizontal projection (Figure 10). Crimp is usually determined by measuring the difference between yarn length in the fabric and its length when unravelled from the cloth and straightened. Crimp values obtained in this manner apply to the unit cell of a plain weave, but must be multiplied by a weave factor, M, when other cloth structures are considered. M is determined from the weave pattern—for example, for warp yarns $\frac{1}{M_w}$ is the ratio of warp crossovers per repeat to the number of filling threads per repeat. M can easily be computed—*e.g.*, in the case of twill constructions one up to the right: a $\frac{5}{5}$ fabric has M equal to $\frac{10}{2}$, or 5; a $\frac{3}{2}$ fabric has M equal to $\frac{5}{2}$, or 2.5; a $\frac{4}{2}\frac{1}{2}$ fabric has M equal to $\frac{9}{4}$, or 2.25.

The sum of the vertical displacement of the crimped path of each yarn system, h, and its diameter, d, will determine which yarns will project at the rubbing surface of the fabric and therefore will be subjected to maximum damage in abrasion [23, 28]. An expression relating yarn displacement, h, to true crimp, c, and yarn spacings, p,

$$h_w = 4p_f\sqrt{c_w}/3,$$

has been found to apply over a wide range of fabric structures [32, 34]. Thus, if the fabric (made of twisted yarns) is designed with a value of $(h_w + d_w) - (h_f + d_f)$ greater than d_w, one may expect the warp to suffer complete abrasive destruction, without damage occurring to the filling.

More recently, a surface coefficient, K_n [11], has been proposed to establish the protruding yarn system based on the fabric geometry. Here $K_n = 0.667 n_w\sqrt{N_w}/n_f\sqrt{N_f}$, where n_w and n_f are the fabric densities in warp and filling directions, respectively, and N_w and N_f are the corresponding warp and filling yarn numbers. Thus, if K_n is less than 1.0, the warp threads protrude at the surface of the fabric; if K_n equals 1.0, the crowns of both yarns lie in the plane of the fabric surface.

In studies of plain weaves possessing high warp and low filling crimp, the curve showing warp strength *vs.* abrasion cycles demonstrates a steep negative slope, indicative of a high rate of damage, while the filling-strength curve is quite flat until the warp is almost worn away [6, 22, 26]. In similar studies [21] dealing with twill, sateen, and herringbone-twill weaves, negligible wear damage is noted in yarns which are buried below the rubbing surface, and, conversely, maximum abrasion takes place on the surface yarns. Evidence of the extent to which damage can occur to one set of yarns while the other remains relatively untouched is presented in a photomicrograph of a horizontal section of an Army poplin material (Figure 11). This photograph demonstrates the extent of abrasive warp damage which may occur before the filling yarns are reached. The usefulness of such longitudinal sections in studying fabric geometry as related to abrasion-resistance has been amply demonstrated [23, 35].

With the importance of crimp distribution established, it is conceivable that the abrasion characteristics of a fabric can be altered by any factor which will modify the crimp balance. Comparisons of fabrics in the loom state with high warp crimp *vs.* fabrics in the finished state, in which the warp crimp has been significantly reduced, have shown significant differences in abrasion performance. Laundering of the finished fabrics and subsequent shrinkage similarly modify crimp distributions, and therefore the abrasion mechanism of the fabric changes [26, 27]; but here the effect of the increased number of threads per inch must also be considered. Finally, slight modifications in fabric construction or weaving conditions—*e.g.*, reed width and warp tensions—may significantly alter the surface of a fabric and its abrasion performance [5]. In effecting crimp changes through control of "in-loom" construction or weaving and finishing conditions, one must have full cognizance of the geometric limitations resulting from yarn jamming [32, 34] and the physical limitations imposed by inherent yarn properties, particularly stiffness. Abrasion experiments have illustrated the importance of this requirement. In one case [27], fabrics were constructed with high filling and low warp crimp, resulting in great damage to the filling in wear and little damage to the warp. In slightly modified constructions, the warp texture was increased, resulting in greater filling crimp. The experimental series was extended until the jamming point was reached, beyond which warp-texture increases simply reduced filling crimp. Just before the jamming point, protection to the warp yarns was noted to be the highest. The protection of the filling yarns, on the other hand, was not at a minimum at this point, because their twisted structure tended to rupture long before the final fiber was worn away. In another instance [6], increased warp tensions in weaving were not sufficient to overcome the jamming which occurred in the constructions selected for study, and weaving conditions were not found to significantly affect wear-resistance. In still another case, it was found advantageous to reduce filling texture so as to enhance warp crimp, thus protecting the loosely twisted filling from surface abrasion [23].

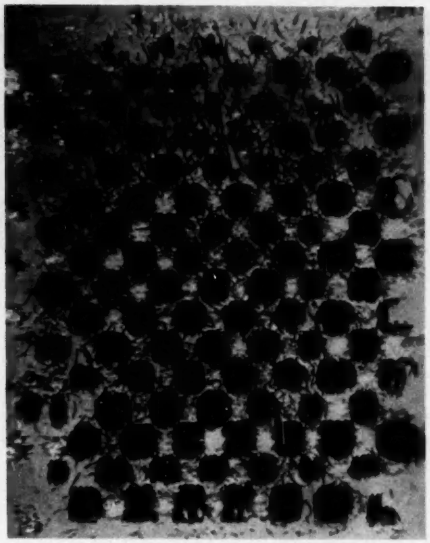

FIG. 11. *Horizontal section of Army poplin.*

In few instances will tension during an abrasion test or during the wear life of a fabric be sufficient to alter the crimp balance in the material [6]. However, wherever the stresses are of sufficient order to reduce crimp in either direction, modified abrasion results may be expected. This is particularly true in novelty and fancy fabrics where long floats at irregular intervals cause a maldistribution of tensile stresses, or where ribs occur, or where intermittent heavy yarns in warp and filling cross one another and create projecting crowns [36]. Thus, it may be expected that a fabric which does not possess over-all dimensional stability will give trouble in laundering, pressing, and subsequent wear.

It is interesting to note that where bursting strengths are used as a measurement of wear damage, crimp distribution affects both abrasion damage and its measurement. In one case reported [8] of a low-warp, high-filling-crimp sateen, bursting strength was found to be a measure of damage in only one system of threads, the low-crimp warp. Thus, when wear took place on the side where the warp was protected by the highly crimped filling, little loss in bursting strength was observed, and vice versa.

Weave as It Influences Projection

In a balanced-yarn, plain-weave fabric constructed with high warp covers (for definition, see [32]), anywhere from $K = 20$ to $K = 30$, the warp threads will bend about the filling threads and little opportunity will be afforded for filling crimp to occur. Even when extra-width reeds are used and the material is subjected to high tensions in the loom or in subsequent finishing procedures, the jammed condition [34] is reached before any measure of crimp redistribution takes place, and the warp remains projected on the surface of the fabric. This is particularly true in tightly woven poplin [55] constructions (Figure 11) where the filling yarns are heavier than the warp yarns, resulting in greater resistance to bending of the former. In such cases, the warp thread projects significantly on both face and back of the fabric, as is pictured in the ideal crimp diagram of Figure 10.

Where twills or sateens are considered, it is evident that many of the assumptions of the simplified cloth geometry no longer apply. The longer the float, the less the restraint on the yarn system. Here yarns are no longer restricted to alternating from one side of the fabric to the other, but bend sideways and allow for the closer packing characteristic of twills and sateens. In particularly long floats, such as are found in the Army five-harness sateen [54], the torus-cylinder form of alternating yarns is modified and a general arclike form is assumed This, when combined with the tendency of adjacent yarns to override one another (see Figure 12), results in higher projection of the yarn system containing the greater number of floats on each side of the fabric, despite the distribution of crimp. This tendency is used to good advantage in protecting from surface abrasion the system of yarns which bears the major stresses during service. In Army utility garments, Kaswell has observed that the longitudinal yarns, normally the warp, bear the major stresses during combat or fatigue activity of the wearer [20]. Damage to the warp is further affected by the relative direction of the yarn twist and of the twill [49], the more pronounced twills suffering earlier loss in strength.

Combat-course tests have shown that the filling-flush sateen [21] offers more protection [38] to warp threads during harsh abrasive wear than does the structure of the herringbone twill. In the case of herringbone twill and sateen arranged so that the filling floats are exposed, filling damage is three to six times that of the warp in the herringbone twill and fifteen to twenty times that of the warp in the sateen. In short, the sateen showed the least warp damage of all the fabrics tested [40]. When cross sections of the fabrics in question are observed (Figure 12), the additional protection afforded the warp by the longer filling float of the sateen becomes evident.

Laboratory tests [21] conducted on sateen, herringbone twill, and uniform twill with reciprocating and rotating type abrasion machines have consistently shown the sateen structure to furnish maximum warp protection when the filling floats are subjected to rubbing. No reversal in this tendency was noted as a result of change in abrasion direction. Conversely, maximum damage occurred to the filling floats of the sateen weave. This is demonstrated in the surface photomicrograph of Army sateen shown in Figure 13. When warp floats are exposed on the rubbing surface, it is seen that the longer floats suffer greater damage [49, 52, 57]—*e.g.*, in the tests on 4/1 sateens, 2/1 twills, and 1/1 taffetas (Figure 1).

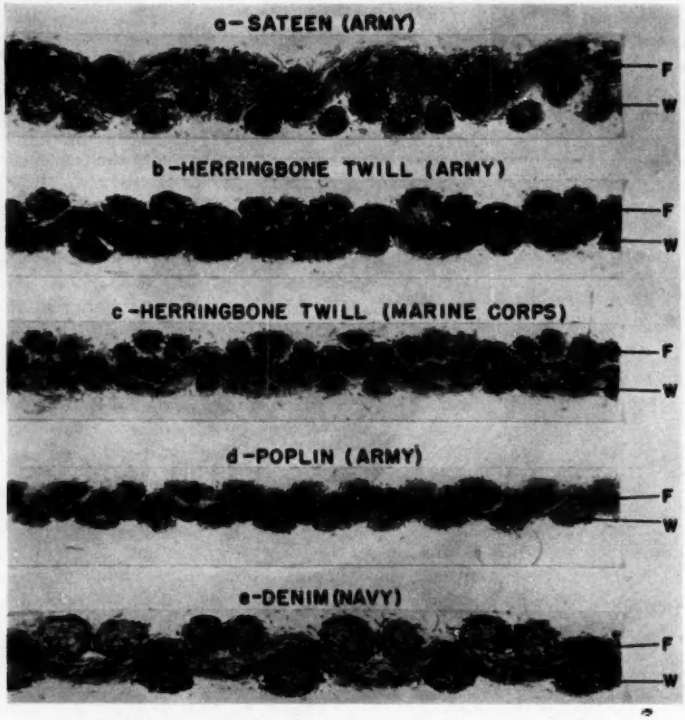

FIG. 12. *Cross-sectional views of various cotton fabrics used by the armed services.*

It has thus been shown to be characteristic of the five-harness sateen that the warp yarns project on one surface and the filling yarns on the other. In tightly woven, high-warp-cover plain or denim (twill) weaves, the warp yarn projects on both face and back and is subject to immediate damage, regardless of the surface abraded. In the herring bone twills, the warp yarns project on the face but are almost flush with the filling floats at the back. The wave height of an alternating yarn is generally related to the relative float lengths of the yarn, for it is evident that the longest float will balloon out

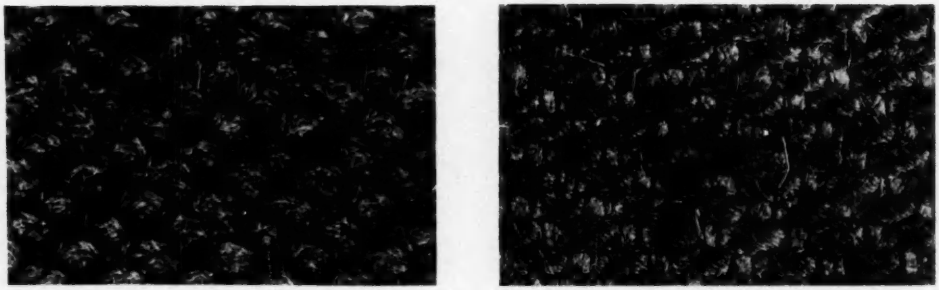

FIG. 13. *Abrasion damage to sateen worn filling flush.* Left—*Abraded.* Right—*Unabraded.*

the most. Measurements of float length in selected experiments [20] are presented in Table II. Here it is shown that the back of the sateen construction has the longest filling float and the highest ratio of filling to warp floats. The warp yarns are to be protected in use, and therefore protrusion of the filling yarn at the outer surface of the fabric is desired.

Comparison between the several fatigue fabrics of the various services has further demonstrated the influence of weave and float length on yarn projection and relative protection of the two systems from surface abrasion. Two herringbone twills were evaluated—one with a float of two cross yarns, the other with a float of three. The other fabrics were a five-harness sateen and a 2/1 denim construction. Details on these fabrics are furnished in Table IV. From Table III it is seen that all of the twills lose significantly in warp breaking strength after reciprocating warpwise rubbing (face up). However, when the fabrics are reversed, the sateen, with the maximum filling float length, is the only material which demonstrates almost complete warp protection under the conditions of abrasion used. This is borne out in Figure 12, where the role of float length and weave in determining yarn displacement is evident.

It has been shown [51] that flex abrasion most nearly correlates with combat-course results on the fabrics described in Table I, for here the abrasion is directed along the warp and the sample reaches the end-point when the warp strength is reduced below the level of the tensile load applied during the test. The flex-abrasion results of Table III (for the back of the fabrics) demonstrates the amount of protection afforded the stress-bearing warp yarns by the filling.

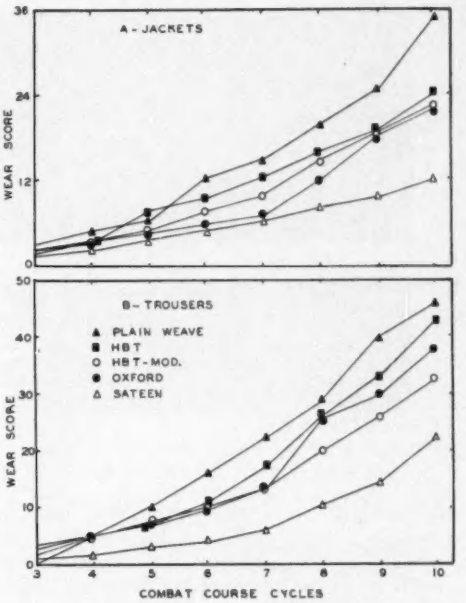

FIG. 14. *Effect of weave variations on combat-course wear scores.*

TABLE II. FLOAT LENGTHS OF SELECTED ARMY FABRICS

		Warp (mm.)	Filling (mm.)
Twill	Face	0.95	—*
	Back	0.26	0.53
Sateen	Face	0.74	—*
	Back	0.26	0.74
Herringbone twill	Face	0.90	0.26
	Back	0.53	0.58

* Not discernible in photomicrograph.

TABLE III. LABORATORY ABRASION TESTS ON COTTON FATIGUE FABRICS

Fabric	Float length (in.)		Wyzenbeek abrasion‡ (% loss in warp strength)		Flex abrasion** (cycles when abraded)	
	Warp*	Filling†	Face	Back	Face	Back
Sateen (No. 111)	.0635	.0476	—	0	—	2029
Herringbone twill 2/1	.0434	.0263	12	6	646	1315
Herringbone twill 3/1	.0600	.0288	19	9	595	1255
Denim	.0426	.0286	23	—	1784	—

* On warp-flush side (computed).
† On filling-flush side (computed).
‡ Wyzenbeek Precision Wear Test Meter, 2-lb. load, 2 lbs. tension, abraded warpwise, 250 cycles.
** Stoll-Quartermaster Abrasion Tester, warpwise flex abrasion with folding bar, 4 lbs. pressure, 4 lbs. tension, 1-in. wide warp strips, end-point cycles to rupture.

TABLE IV. PHYSICAL PROPERTIES OF STANDARD SERVICE FABRICS

Construction	Army Sateen	Army Standard HBT	Marine Corps HBT	Navy Denim
Weave	5-harness	HBT 2/1 12 ends right 12 ends left	HBT 3/1 16 ends right 16 ends left	2/1 twill
Weight (oz./sq.yd.)				
Experimental	10.2	8.9	9.4	10.0
Theoretical			9.3	9.9
Texture				
Ends/in.	84	76	104	70
Picks/in.	63	46	50	47
Yarn number, singles cotton				
Warp	13	13	17	8.5
Filling	10	8	8.2	13.2
Cover factor, K_w	23.0	21	25.0	24.0
K_f	20.0	16	17.0	13.0
Yarn crimp (%)				
Warp	12.3	11.8	12.6	27.6
Filling	14.6	11.3	10.2	10.2
Physical Properties				
Breaking strength (lb.)				
Warp	154	140	130	160
Filling	136	146	134	70
Tearing strength (lb.)				
Elmendorf, Warp	10.9	5.9	8.2	10.0
Filling	12.0	7.5	9.4	4.5
Tongue, Warp	10.7	3.8	6.2	—*
Filling	7.7	4.9	7.4	3.0
Thickness (0.001 in.)	26.4	19.5	20.4	25.8
Stiffness (0.001 lb.)				
Warp	3.1	3.8	3.7	13.0
Filling	3.6	3.6	4.2	5.4
Air permeability (ft.³/min./ft.²)	9.8	21.4	14.9	18.0
Wear score, revised (Camp Lee)	8.0	23.0		
Warp yarn in the left twill—Z twist Warp yarn in the right twill—S twist				

* Did not tear in warp. Tore across the filling.

The most striking example of this warp-protection mechanism is seen in the results of combat-course tests plotted in Figure 14 and summarized in Table I. The plain-weave fabric possessing tight warp crowns and with a filling float length of one crossover has the poorest (highest wear score) resistance, while the sateen with a filling float length of four crossovers has the best. Intermediate wear scores are evidenced in the herringbone twills and the Oxford fabric, which have the filling float passing over two cross yarns. As Kaswell pointed out [21], the important part of this geometric consideration is the protection of the tensile stress-bearing yarns, which in the case of combat-course wear are the warp yarns. Other considerations, such as that of yarn mobility, are present, but these are discussed later (p. 649).

Finally, it should be stressed that irregularities in the weave pattern should be avoided to prevent one portion of the repeat from projecting above the

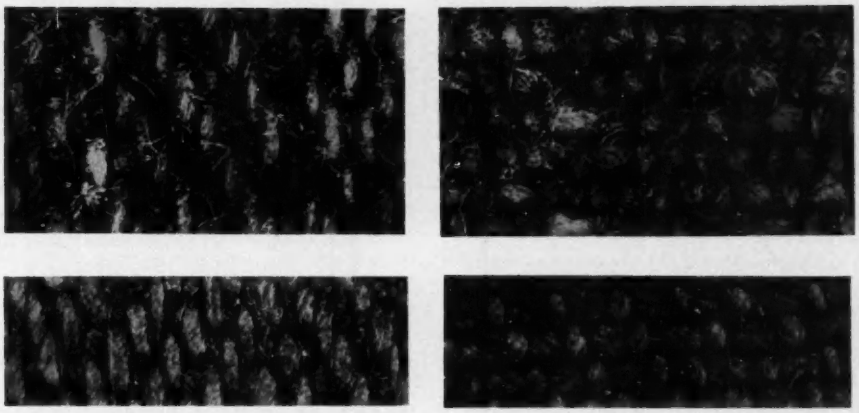

FIG. 15. *Abrasion of projecting floats of herringbone twill.* Top—*Abraded samples, face (left) and back (right).* Bottom—*Unabraded samples, face (left) and back (right).*

other and receiving the brunt of the wear. An example of this is seen in the herringbone-twill fabric, in which at one point in the repeat the length of the filling float is reduced by 50%. This throws the warp thread crossing the filling at this point out of the plane of the fabric surface and subjects it to excess wear at an early stage, as is evident in Figure 15 (left). At another point in the herringbone twill, where a filling float is increased by 50%, causing it to arch out of the plane of the back surface of the fabric, maximum wear is again noted (Figure 15, right).

Twist as It Influences Contact Area

The importance of cohesion of fiber, yarn, and fabric has been stressed by many investigators of the wear phenomenon [32, 51]. It has been shown that the surface wear of fabrics can consist of fiber damage, with either partial or complete rupture of the individual hairs, or a plucking of the fiber from the yarn structure [6, 57]. For good wear, the tearing-out action can be reduced by a firm binding of the fibers [28]. This binding may be accomplished by increasing yarn solidarity, with higher twists, or by use of tighter weaves. When twist multiples are increased from 1.5 to 2.3 in the yarns of linen fabrics, an increase of 15% in abrasion-resistance has been reported [27], and it was thought that the harder, more highly twisted yarns had less contact with the abrasive surface and so suffered less damage at the surface fibers. Based on results of more recent yarn tests, it would appear that lower twists afford poor fiber binding while high twists stiffen the yarn to a point where there is very little contact between yarn and abrasive. This, in turn, results in high local abrasive pressures and early breakdown of the yarn structure. However, when materials are laundered to a greater extent than abraded, the poor fiber binding of low-twist yarns plays a major role in causing early breakdown. Here, higher yarn twists are more durable [14]. In the experiments with viscose materials [18], an optimum twist is recorded beyond which increases in the number of turns per inch result in lower abrasion-resistance. The curves of abrasion-resistance *vs.* twist follow the pattern of the well-known, tenacity-twist curves [37]. It is seen, therefore, that the compressional characteristics of a yarn and its cohesiveness play dual roles in determining abrasion-resistance as its twist is altered. It follows that different abrasion behavior may be expected in fabrics of varying yarn twists, depending upon the normal loads between the rubbing surfaces.

In considering end-points, twist is a significant factor in determining the loss in yarn strength which may be expected for a given depth of cut at the crown of the yarn float. Yarn twist brings different fibers to the surface in any float length. The number of different fibers at any surface will depend upon the float length, the turns per inch, and the fiber and yarn diameters [37, 45]. In many instances, all of the fibers lying a given depth (abraded

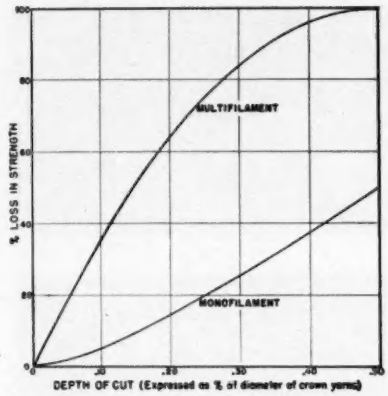

FIG. 16. *Relationship between depth of cut and % loss in strength of multifilaments and monofilaments.*

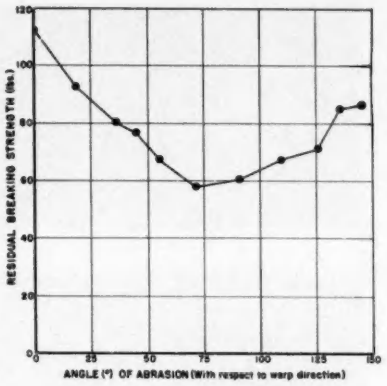

FIG. 17. *Effect of direction of rubbing on the abrasion-resistance of Army poplin.*

depth of crown) from the yarn surface rise to the surface at each float or at adjacent floats, thus degrading yarn strength by an amount proportional to their cross-sectional area. Platt [37] pointed out that when this loss is compared to the loss of strength at the same depth of cut in a monofil yarn, the relationship plotted in Figure 16 is seen. It is further noted that the strength loss of the monofilament is, in fact, directly proportional to the volume of yarn removed and therefore to the loss in weight during abrasion. In fabric-abrasion tests, these same relationships have been observed between loss in weight of the specimen and loss in strength [6].

Combat-course evaluations of the wear-resistance of fabrics differing only in yarn twist have been limited to tests of 2/1 twill weaves. Three of these fabrics had different twist multiples in the warp—namely, 4.25, 4.75, and 5.25—while the filling twist multiples were kept constant at 3.75. The other fabrics had warp twist multiples of 4.75 and filling twist factors of 3.25, 3.75, and 4.25, respectively. The combat-course tests showed a very slight, though consistent, improvement in fabric wear (in both test series) as the twist multiples of either warp or filling yarns were increased in the range indicated. All of the twills tested had the twill line running up to the right, with the exception of one left-hand twill. There was no difference noted between the wear score of the left-hand twill and a comparable fabric in a right-hand twill.

Direction of Abrasion

Major differences exist in the abrasion performance of textile fabrics when the direction of rubbing is altered with respect to warp and filling coordinates [27, 46]. The advisability of analyzing field wear to establish the predominant direction of wear and stress has been noted in early abrasion studies [6, 23]. In experiments where fabrics have been rubbed in warp and filling direction, a ratio as high as 2:1 has been observed in the number of strokes required to form a hole [8]. Generally, the yarns which project on the rubbing surface of the fabric will suffer the greatest damage when abrasion takes place in a direction perpendicular to their float lengths [17, 21, 28, 47]—*e.g.*, Figure 17. Where it is evident that abrasion and tensile stresses occur in one direction, it is desirable to increase the perpendicular set of yarns as to frequency and diameter and bring them to the surface to absorb the wear [20]. Under these conditions, unfortunately, the cross yarns absorb maximum damage during a period of rubbing. Maximum resistance is achieved when the non-stress-bearing yarns are presented at the rubbing surface with their floats running in the direction of rubbing [28]. Since the direction of service wear and stress is often the same, the maximum abrasion life of the fabric is not often realized. Wherever possible, however, the design of the garment or lay of the fabric in the pattern should be altered so as to eliminate perpendicular rubbing of the surface yarns during the wear of the item.

This is more easily accomplished in the manufacture of fatigue garments for Army use than of dress uniforms or civilian clothing. One feature that can be modified quite easily is the exposure of face or back of the material to the rubbing element, depending upon which side exposes the nonstressed yarns. Fabric reversal of this nature is resorted to in a number of Army garments.

Mention has been made of the two types of breakdown which occur in fabric wear [28]: the loss in internal cohesion of the fiber and the loss in structural cohesion between fibers. The relative occurrence of these two phenomena depend to a great extent upon the structural compactness of yarn and fabric, and upon the direction of abrasion with respect to surface yarns. Abrasion directed along the yarn in tight, sharp-knuckled fabrics often results in a great many sheared fibers. Abrasion directed across these same yarns tends to snag the fibers, leaving a hairy surface after a few rubs. Studies conducted in the Quartermaster laboratories on weaves of different float lengths demonstrated varying degrees of damage on warp and filling yarns, depending upon the nature of yarn projection, the float length, and the direction of abrasion. Abrasion, in this case, was of short duration so as to permit microscopic evaluation of the initial stages of surface wear before the destruction progressed to a point where it was impossible to distinguish between the types of mechanical breakdown and to assign damage to specific yarn systems. To extend the usefulness of this technique, it is, of course, necessary to study surface disturbance on fabrics whose structures have been brought to equilibrium in laundering. Another technique used to good advantage in studying surface structure of Army fabrics is the three-dimensional photography or vectograph process.

Compliancy

Relationship to Compressional Properties

The influence of backing materials in abrasion testing is well known, although little is reported in the literature since most investigators arbitrarily standardize the type of backing used in a given test. The various degrees of backing softness on a man's body have an effect on the relative wear of different portions of his garment. This factor is believed to play an important role in the variation in wear scores recorded in combat-course tests of Army clothing, although another factor which must be considered at the same time is the wearing habit of the individual—that is, what portions of his body he brings into contact with the different abrasive elements during traversal of the course. Soft backing, extra padding thickness, or napping of the fabrics in test add to the compressive give, and thereby to the ability to escape damage at the abrading surface [13, 19, 25, 49].

Finally, it is concluded that the compressive behavior of the surface structure itself bears on its wear performance, and it may be expected that a low compressive modulus and high rate of recovery will enhance abrasion-resistance, reducing the normal pressures at local protuberances.

Relationship to Fabric Tightness

Reduction in the extent of fiber plucking during wear, by closer weave or high twist, should not be effected at the expense of local rigidity at the fabric surface. There is sufficient evidence to demonstrate that tightly woven, knuckled fabrics possess low wear-resistance [21, 40, 58]. This is caused by the inability of the surface fiber to translate and avoid the path of the abradant particle. As a result, stresses are set up in the fiber which may exceed the multidirectional shear or tensile strength at the localized point of contact, or the axial tensile tenacity in the case of macrosnagging [49]. In general, the mobility required to alleviate surface stresses on individual fibers can be achieved by flattening the yarn structure in compression, as indicated above, or by rotation of the yarn, or by yarn translation within the fabric structure.

The use of lubricants has often been proposed as a means of increasing yarn mobility and thus of extending the wear life of textiles. It has been the experience of the Quartermaster laboratories that small percentages of lubricants may be beneficial to the abrasion life of cotton fabric as measured in the laboratory, but this is not always borne out in service. In one of three field tests in which the Quartermaster Corps participated, improvement of the treated fabric was noted to be due, in part, to the reduced laundering resulting from the stain-resisting character of the lubricant. In the other tests where uniform laundering procedure was followed, little difference existed between treated and untreated materials after extended periods of use. Lubricants have been found to be extremely useful in reducing the amount of thread damage occurring during the sewing operation. It has, in fact, been

possible to sew with a high degree of seam efficiency fabrics which in the unlubricated state were badly perforated in the manufacture of shirts and were torn as easily as paper. Textile lubricants are generally looked upon as enhancing fiber and yarn movement within the fabric. They contribute in varying degrees to increased sewability, more seam slippage, higher laboratory abrasion-resistance, and, on occasion, improved wear life in service.

For the case of macrosnagging, the amount of yarn rotation depends upon yarn twist and fiber tensile modulus, for these factors determine the torsional rigidity of the yarn. If the yarn rotates enough to permit the surface fiber to slip from under the abrasive asperity, little immediate damage will occur, although long-time cumulative effects may be present, such as removal of secondary creep and bending fatigue. However, if the surface torque developed during yarn rotation is of such a magnitude as to cause fiber rupture, damage will be evident after the initial passes of the abradant surface over all parts of the fabric. To avoid excessive torques, one may use a fiber of lower tensile modulus or a yarn of lower twist. Finally, the use of longer floats (assuming the same torsional rigidity of the yarn system) reduces the magnitude of stress at the surface fiber.

In repeated impacts of the abradant, it is important that the fiber and yarn return to their original positions before approach of the second particle. If struck while in the rotated position, the higher twist of the yarn will effect a higher torsional rigidity and will therefore cause an increase in the force at the newly exposed surface fiber before the necessary rotation for clearance of the abradant particle can take place.

It follows that the ability of the yarn to recover its original position before the approach of subsequent abradant particles significantly affects its wear-resistance. This recoverability is related to: the inherent immediate elastic properties [16] of the fibers; the twist of the yarn; the distribution of sharp particles on the surface of the abrasive; the relative velocity between abradant and specimen (extent of rest periods); the path of the abradant across the specimen [7, 44].

In field tests the material is often allowed to recover after abrasive treatments, and thus heat of friction is disposed of and primary creep is recovered so that yarn and fiber assume a position near to their original state. In laboratory tests, however, there is no allowance for the time factor and for relaxation between cycles [10, 50], and materials which cannot recover in time for repeated abrasive runs tend to have low abrasion-resistance. Under modified conditions of abrasion, it is likely that rankings may be easily reversed because the influence of yarn compliance is weighted differently.

Fabric compliance depends upon the threads per inch and the type of weave. Geometric studies have shown that the number of picks which may be woven in a fabric is limited by the number of warp ends per inch, assuming fixed yarn sizes. The limiting construction of picks for a given sley, or vice versa, is known as the jammed condition [32, 34]. The quantitative expression of tightness as the ratio of actual picks (or ends) per inch to the maximum number per inch for a given cover factor, K, in the opposite direction is quite useful in fabric development. It will be recalled that cover factor is the ratio of threads per inch to the square root of the yarn count (cotton system). For plain weaves [32]:

$$K_w = \frac{28}{(1 + \beta) \sin \theta_f}$$

$$K_f = \frac{28}{(1 + \beta) \sin \theta_w}$$

$$1 = \cos \theta_w + \cos \theta_f$$

for the jammed condition, where $\beta = \sqrt{N_w/N_f}$ and θ is the angle of inclination of the yarn system at the central plane of the fabric, as seen in Figure 10. If two of the five unknown quantities in the above three equations are selected arbitrarily, the remaining three quantities can be determined easily. For example, if the ratio of yarn diameters and the warp cover factor are known, one can solve to find the limiting pickage of the jammed structure and the inclinations of the yarns systems.

In considering weaves other than the plain weave, one must correct for differences in the intersections between yarns. This can be done by adjusting the measured cover factors for each weave and using the values which have been corrected in the above expressions. The formulas for cover-factor adjustment are as follows:

$$K_w' = \frac{1}{\frac{M_f}{K_w} - \frac{(M_f - 1)f_w}{28}};$$

$$K_f = \frac{1}{\frac{M_w}{K_f} - \frac{(M_w - 1)f}{28}},$$

where K is the measured cover factor and K' the corrected cover factor, M is the weave factor, and f is the relative degree of flattening of the yarns, expressed as a ratio of major axis of flattened yarn to diameter of round yarn of the same count. While the original cover factor is related to the tightness of yarn in a given direction, exclusive of the effect of cross yarns, the modified cover factors are related to combined tightness, taking both sets of yarns into account. Within the practical ranges of weave factors and measured cover factors, M_f and K_w can be increased together without affecting K_w'. For example, if the maximum desirable tightness, K_w', is 15 and the flattening factor, f, is 1.4, then for a weave factor of $M = 5$ the actual warp cover factor is $K_w = 18.7$; for $M = 2.5$, as in the case of a five-harness sateen, $K_w = 17.7$; for $M = 1$, as in the case of a plain weave, $K_w = 15$.

The cover factor of the threads which protrude at the surface is the primary factor in determining the geometric area of contact of the fabric with the abradant, while the modified cover or tightness factor reflects the extent of mobility afforded the protruding yarns by the fabric geometry. It follows that fabrics with high values of M can pack considerably more yarn per unit area without increasing fabric tightness, thus avoiding reduction in abrasion-resistance through loss of mobility. Meanwhile, the increased bearing surface of the higher-textured fabrics results in reduced abrasive pressure per crown or float and less abrasive damage. Conversely, when textures are kept constant, the M values of a given structure determine yarn mobility and therefore are a measure of the ability of the yarns to redistribute stress concentrations in abrasion and also in tearing or snagging. In Table I and Figure 14 the sateen fabric with the weave factor of 2.5 in both warp and filling shows the maximum (of group II) abrasion-resistance and tear-resistance, together with the lowest tensile (strip) strength. The plain-weave fabric with M_w, $M_f = 1$, 1, respectively, shows the poorest abrasion- and tear-resistance, while the herringbone-twill and Oxford fabrics with weave factors M_w, $M_f = 1.5$, 1.5 and 1, 2, respectively, show intermediate values of tear- and abrasion-resistance. This ranking has been attributed to the protective protrusion of the longer filling floats, but it is highly probable that yarn mobility plays a significant role in determining the relative abrasion life of the fabrics whose warp yarns protrude at the rubbing surface—in this case, the plain, Oxford, and herringbone twills. Obviously, there is a limit in float length at which increased snagging of the protruding yarn vitiates the advantages of longer floats. In addition, the conditions of abrasion may be such that the yarn mobility may be inoperative—for example, as a result of fine abrasives moving at a high speed over the surface of the fabric. An instance of this is seen in the poor showing of the sateen construction in laboratory tests under conditions where compliance and recoverability are reduced in importance. Results of this sort [52] appear at first glance to be anomalous, and such anomalies continue to appear in any abrasion-testing program. It is therefore incumbent upon the individual investigator to see that the conditions of abrasion testing [5] are related to service conditions and that laboratory testing is confirmed, wherever possible, by service trials [8].

An important approach to the problem of reproducing service conditions is the study of worn garments from varied groups of consumers. Here is found valuable evidence of the nature of actual wear and clues as to the type of laboratory tests that are best suited to predict the type of service performance for particular usage. Here, too, is observed weak spots in fabric structure, finish, manufacturing technique, seam and stitch construction, thread quality, and garment design. Such surveys [4, 39] conducted during and after the war serve as the basis for improvement of Army fabrics and garments.

Development of improved laboratory abrasion equipment has been a successful part of this program [43, 51], and although there is confidence in the results obtained with these instruments, further work in their evaluation is still necessary. The variables indicated above emphasize the need for extreme caution in attempting to predict the performance of new fibers, fabric constructions, or finishes under conditions of service which have not been thoroughly studied for presently available textile materials.

Conclusions

The geometric area of contact between cloth and abradant surfaces determines the magnitude of local pressures occurring under a given abrasive load. Local pressures, in turn, influence first the depth of local penetration into the fabric structure by the abradant asperity, and then the true area of contact

between cloth and abradant. The local penetration controls the magnitude of cutting and snagging damage, while the true area of contact determines the amount of frictional damage which takes place in the form of fiber slippage and/or fatigue. In short, the geometric area of contact between cloth and abradant determines the rate of fabric attrition during rubbing. This area can be increased in the normal course of designing a textile fabric, the simplest method being the use of higher cover factors and equal crown heights in warp and filling. Increased cover factors may be achieved through higher textures or coarser yarns. Crown heights can be equalized by adequate control of crimp. In addition, the use of lower twists is an alternative method of increasing contact between individual yarn crowns and the abradant. Finally, the total abrasion-resistance or wear life of cloth is related to the thickness or diameter of that element of the textile structure which is exposed at the rubbing surface.

The above modification of fabric structures can be carried out only within limited ranges, else their beneficial effects are offset by secondary factors. For example, if fabric textures are increased excessively, yarn mobility will be severely reduced and rigid knuckles will form which are incapable of absorbing abrasive energy without early failure of surface fibers. Use of overly large-diameter yarns in one direction and small-diameter yarns in the perpendicular direction will result in the lighter set bending freely while the heavier, stiffer set remains uncrimped. This condition will lead to an actual reduction in the geometric area of contact and to early damage to the exposed, lighter yarns. Yarn cohesiveness may be so reduced by use of low twist that excessive damage may soon occur through the snagging and slippage of loosely bound surface fibers.

In many cases, fabrics are subjected to both abrasive and tensile stresses during their use. In designing more durable cloth to meet the requirements of the above conditions, it is recommended that strong yarns be used in the direction of applied stresses and that these yarns be buried below the exposed surface. Protection of the stress-bearing yarns may be effected by the control of crimp in the design and manufacture of the cloth. Geometric relationships in plain-weave fabrics have been developed to the point where the relative protrusion of one system of yarns above the other can readily be designed and implemented in the course of fabric weaving and finishing. Twills and sateens do not meet the simplified assumptions of the plain-weave geometry; however, a first approximation in the design of short-symmetric-float weaves may be made by applying correction factors to the geometric relationships of the simpler structure. These methods break down in the case of the long-nonsymmetric-float weaves where cover factors are roughly balanced. This is explained by the fact that the long component of the nonsymmetric float will balloon out on one side of the fabric while its short component is buried on the other side. Of the two methods of burying the stress-bearing yarns —through crimp control and through the use of the long nonsymmetric float—the latter is preferable in the design of wear-resistant fabrics. It is simply not practical in the full-scale production required by Army procurements to attempt to set crimp specifications for the finished cloth.

Maximum damage in wear of a fabric will occur when the direction of rubbing is perpendicular to the exposed floats. It is therefore desirable to orient the fabric in the design of clothing, so that exposed floats are parallel to the predominant direction of rubbing. Unfortunately, this is not possible where abrasion and tensile-stress directions coincide, as in the case of Army fatigue garments.

Fabric durability is enhanced by increasing the compressive compliance at the rubbing surface. This may be done by modification of the structure of the cloth itself or by use of soft backing materials. Local yarn compliance is also important to promote stress distribution at points of contact, and it must be retained within limits when high cover factors are utilized to increase the bearing surface. Where high cover factors are required for purposes of water- or wind-resistance, it is desirable to utilize structures with higher weave factors (*i.e.*, with fewer intersections per unit area) in order to avoid jamming and knuckling of yarn crowns.

The above conclusions are admittedly qualitative and cannot be used to design a fabric from scratch to meet a specific end-use or to predict its wear life. Their value lies in their application to end-use problems where limited experience and quantitative information are already available. Here they serve to explain the reasons for low durability-weight ratios and point the way to significant improvements in wear-resistance consistent with other structural requirements. This report provides a background

of quantitative data for selected fabrics and uses as reported previously in the literature and more recently developed in military studies. It is hoped that the reasoning presented here can be used as effectively in future civilian research as it has in past military programs.

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Modification of Wool by the Application of Linear Synthetic Polyamides

Part II: *N*-Hydroxymethyl Polyamides*

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Abstract

The effect of surface deposits of *N*-hydroxymethyl polyhexamethylene adipamide on the felting shrinkage of wool has been determined. These polymers resemble the *N*-methoxymethyl polyamides in that the polymer itself is not particularly effective in preventing felting shrinkage of wool, but when the substituted polymer is applied to wool fabric and then converted to the unsubstituted polyamide on the fabric, its effectiveness in reducing felting shrinkage is very much increased.

A deposit of approximately 3% by weight of polymer on the fabric has been found to eliminate entirely felting shrinkage of the fabric under the test conditions. The optimum degree of substitution of the polyamide for production of non-feltability is similar to that found for the *N*-methoxymethyl derivatives—*viz.*, between 20% and 25% —NH groups substituted.

The *N*-hydroxymethyl polyamides can be converted to the unsubstituted polymers either by hydrolysis—*e.g.*, with acids—or by heating in air.

Introduction

The ability of wool fabrics to felt is considerably reduced by treatment with a solution of *N*-methoxymethyl polyhexamethylene adipamide, followed by acid hydrolysis to the unsubstituted form of the surface deposit of polymer on the fabric [4]. Although felting is eliminated by a deposit of unsubstituted polyamide, the same effect cannot be obtained by simple application of the polyamide itself—it is necessary to apply the substituted polymer first and then hydrolyze it on the fabric.

The substituted polyamides used in Part I [4] contained little or no hydroxymethyl (—CH_2OH) substitution, the substituent groups being almost entirely methoxymethyl (—CH_2OCH_3). It is reasonable to assume that *N*-hydroxymethyl polyamides will act in a similar way to the *N*-methoxymethyl polymers, because they are soluble in aqueous ethanol and can be hydrolyzed by acid even more readily than the latter. Further, they can be made insoluble in alcohol by heating in air, and this offers an alternative to the acid-hydrolysis treatment. The effect of *N*-hydroxymethyl polyhexamethylene adipamide polymers of varying degree of substitution on the felting properties of wool fabric has therefore been investigated after both acid and heat treatments.

Materials and Methods

Polyhexamethylene Adipamide

Waste commercial nylon hosiery yarn was used after being purified as described in Part I [4].

N-*Hydroxymethyl Polyhexamethylene Adipamide*

A number of samples of the *N*-hydroxymethyl polymer of differing degrees of substitution were prepared from the above nylon by the method of Cairns *et al.* [1, 3] using the following general procedure: 30 g. of nylon yarn was dissolved in 180 g. of 90% formic acid at 60°C, and the required quantity of formaldehyde solution (either 36% formalin solution or a solution of paraformaldehyde in water) was added slowly, at 60°C, with stirring. After 10 min., the solution was poured into 1 l. of acetone

* Part I appeared in the March, 1951, issue of TEXTILE RESEARCH JOURNAL, page 156.

containing sufficient ammonia to neutralize the formic acid, and the polymer which separated was washed until free from acid, and then dried under vacuum, over phosphorus pentoxide, at room temperature.

The molar ratio of formaldehyde to nylon was varied from 5:1 to 20:1, and a corresponding range of samples containing from 4.9% to 6.7% combined formaldehyde obtained.

Wool

The fabric used in all treatments was prepared from 64's quality wool and had the following construction:

Weave	Mayo twill
Warp yarn	33's Yorkshire skeins
Weft yarn	30's Yorkshire skeins
Ends/in.	32
Picks/in.	30

The fabric was extracted with ether, alcohol, and distilled water before use.

Determination of Combined Formaldehyde

Combined formaldehyde was estimated by the method of Clasper and Haslam [2] as follows: About 2 g. of polymer was heated under reflux on a water bath at 60°C with 80 ml. water and 2 ml. sulfuric acid for 2 hrs. The acid was then neutralized with *N* sodium hydroxide solution; 50 ml. of *N* sodium sulfite solution was added; and after 5–10 min. the liberated alkali was titrated against approximately 0.5 *N* hydrochloric acid, using thymolphthalein indicator. After correcting for the alkalinity of the sodium sulfite solution, the combined formaldehyde was calculated from

$$\% \text{ H·CHO} = \frac{\text{ml. } 0.5N \text{ HCl} \times 1.501}{\text{wt. of sample}}.$$

Determination of Felting Shrinkage

Most shrinkage tests were carried out in a wash-wheel apparatus, as previously described [4]. Some tests, however, were made in a commercial rotary washing machine using 0.05% soap solution at 37°–40°C. The marked fabric samples were washed for about 10 min. in the machine, when about 40% area shrinkage of the untreated samples was obtained.

As the wash-wheel and the washing machine were found to give comparable results for two sets of treated samples, the two methods are interchangeable. An advantage of the washing machine is that it can take larger samples and a greater number of samples than the wash-wheel.

Treatments and Results

All samples were allowed to condition before and after treatment at 65% R.H. and 70°F, and were then weighed. The polymer content of the samples is expressed as a percentage increase in weight based on the initial weight of fabric.

Effect of Substituted Polymer on Felting Shrinkage

Small squares, approximately 6 in. × 6 in., of the wool fabric were immersed for a few minutes in a solution of *N*-hydroxymethyl polyamide (5.8% H·CHO) in 90% aqueous ethanol. They were removed from the solution, mangled, and allowed to dry in air. The original 5% solution was progressively diluted with 90% ethanol after each immersion of fabric in order to obtain a series of samples containing varying amounts of polymer. The fabrics were immersed in water, mangled, and allowed to condition. Felting-shrinkage results of these samples are given in Table I.

Acid Hydrolysis of Polymer

As *N*-hydroxymethyl polyamides are generally more easily hydrolyzed than *N*-methoxymethyl derivatives, it would be expected by analogy with results previously obtained for *N*-methoxymethyl polyamides that acid treatment of fabrics treated as above would considerably reduce this tendency to felt.

Fabrics treated as above with *N*-hydroxymethyl polyamides of differing degrees of substitution were immersed in 2*N* hydrochloric acid at 25°C for 30 min. They were then washed in running water until free from acid, and were allowed to condition.

TABLE I. EFFECT OF *N*-HYDROXYMETHYL NYLON ON FELTING SHRINKAGE

% Polymer on fabric	% Felting shrinkage
16.0	3
12.0	5
8.7	12
7.6	12
7.5	16
6.8	16
5.6	25
5.8	26
4.8	28
0	40

The effect of these polymers on felting shrinkage is given in Table II.

Heat Treatment of Polymer

An alternative method of modifying the *N*-hydroxymethyl polymer in order to increase its rigidity is to heat in air. This causes liberation of formaldehyde; the polymer probably reverts to the unsubstituted form.

Preliminary experiments were made to determine the conditions of heating necessary to render the polymer insoluble in alcohol. The polymer was deposited on samples of fabric from aqueous ethanol solution, as described above, and the fabrics were heated in an air-oven for varying times and temperatures. They were then extracted in boiling 90% aqueous ethanol, and the loss in weight determined.

The results (Table III) show that insolubility in alcohol was produced only after heating at 120°C.

The two samples which were heated at 120°C were further extracted with 90% formic acid at 25°C, and all of the polymer deposit was removed. This suggests that little, if any, cross-linking of the polymer takes place during heating, the main reaction being loss of formaldehyde. During heating, the odor of formaldehyde is easily discernible.

For subsequent experiments, samples of fabrics containing deposits of various *N*-hydroxymethyl

TABLE II. EFFECT OF *N*-HYDROXYMETHYL POLYAMIDES, AFTER ACID HYDROLYSIS, ON FELTING SHRINKAGE OF WOOL FABRIC

Degree of substitution as % H·CHO	% Polymer on fabric	% Felting shrinkage
4.9	4.3	0
	3.8	0
	2.8	3
	2.3	9
	2.1	22
	1.8	33
	0	40
5.6	2.5	7
	1.6	16
	1.0	32
	0.8	30
	0.7	33
	0	40
5.8	4.4	0
	4.3	0
	3.1	0
	2.3	5
	1.7	8
	0.8	34
	0	40
6.6	3.7	7
	3.5	14
	2.4	26
	1.2	34
	0.7	36
	0.7	36
	0	40
6.7	4.9	0
	4.4	3
	3.7	11
	2.4	20
	2.2	31
	2.1	29
	0	40

TABLE III. HEAT TREATMENT AND ALCOHOL EXTRACTION OF *N*-HYDROXYMETHYL NYLON

Time (min.)	Temperature (°C)	% Polymer on fabric: Before extraction	% Polymer on fabric: After extraction
15	120	3.5	3.6
30	120	3.6	3.7
15	100	3.9	nil
30	100	3.9	nil
15	80	3.5	nil
30	80	4.0	nil
no treatment		3.8	nil
no treatment		3.9	nil

TABLE IV. EFFECT OF *N*-HYDROXYMETHYL POLYAMIDES, AFTER HEATING AT 120°C FOR 30 MIN., ON FELTING SHRINKAGE OF WOOL FABRIC

Degree of substitution as % H·CHO	% Polymer on fabric	% Felting shrinkage
4.9	4.5	0
	3.2	2
	2.9	3
	2.6	18
	2.2	21
	1.9	31
	0	40
5.6	2.6	8
	1.9	16
	1.4	24
	1.2	28
	1.0	29
	0.8	33
	0	40
6.7	4.2	0
	3.6	5
	3.1	10
	2.6	15
	2.2	32
	1.9	26
	0	40

polymers were heated at 120°C for 30 min., immersed in water, and conditioned before weighing.

The effect of this treatment on felting shrinkage is given in Table IV.

Discussion

The results of Tables I, II, and IV are plotted in Figure 1. As the range of substitution of the various samples is small, the points fall close together on the graph, but it will be seen that they are in two main groups: those for samples with a degree of substitution of 5.6% or 5.8% (expressed as % combined formaldehyde); and those with 6.6% or 6.7% combined formaldehyde.

From these results, it is seen that the effect of *N*-hydroxymethyl polyamides on the felting shrinkage of wool fabric is very similar to that of the *N*-methoxymethyl derivatives. The polymer itself has little effect in reducing felting shrinkage, at least 16% polymer on the fabric being necessary to prevent felting. This amount is of the same order as that required of many other resins which have been described for the prevention of felting by surface deposition; it is useless for practical purposes, since such a large resin deposit would alter completely the desirable character of the fabric.

When the original polyamide is regenerated, by acid hydrolysis or by heat, from the substituted polymer, after being applied to the fabric, the polymer is very effective in preventing felting with as little as 3% polymer on the fabric.

The action of heat is as effective as the action of acids on the *N*-hydroxymethyl polyamide, as is seen from Tables II and IV. In Figure 1, results obtained by both acid hydrolysis and heat treatment for polymers containing 4.9%, 5.6%, and 6.7% combined formaldehyde are plotted together.

The explanation of these results is thought to be as previously given [4]. The substituted polymers, unlike the regenerated polyamides, are not sufficiently rigid to prevent felting during the washing test. Further, since a deposit of nylon applied from formic acid is not so effective as the nylon deposits obtained by the method described here, it is assumed that the function of the substituted polymers is to reduce the intermolecular cohesion of the nylon, and so allow it to spread to a greater extent on the wool fabric.

The optimum degree of substitution of the polyamide used appears to be similar for both *N*-methoxymethyl and *N*-hydroxymethyl polymers—*viz.*, between 5% and 6% combined formaldehyde,

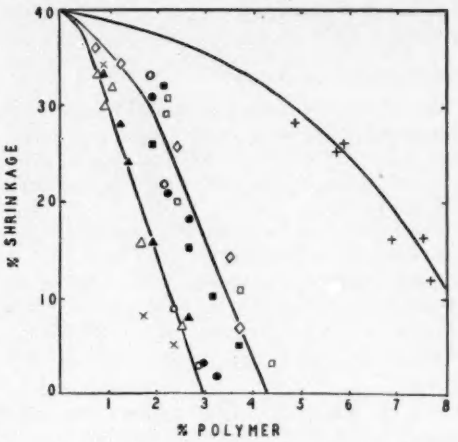


FIG. 1. *Effect of N-hydroxymethyl polyamides on felting shrinkage of wool fabric.*

Sample	*Degree of substitution as % H·CHO*	*Subsequent treatment*
+		*none*
○	*4.9*	*acid*
●	*4.9*	*heated*
△	*5.6*	*acid*
▲	*5.6*	*heated*
×	*5.8*	*acid*
◇	*6.6*	*acid*
□	*6.7*	*acid*
■	*6.7*	*heated*

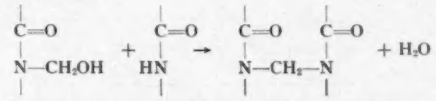
or about 20%–25% —NH groups substituted. As the degree of substitution is increased above these values, the effectiveness of the polymer in reducing felting shrinkage tends to decrease.

Although 2*N* hydrochloric acid has been used for hydrolysis of both *N*-hydroxymethyl and *N*-methoxymethyl polymers, other acids can also be used. The rate of hydrolysis of the polymer depends upon the temperature, concentration and type of acid used, and the thickness of the polymer film. The latter, which determines the rate of diffusion of the acid through the film, is probably the controlling factor.

Other agents may be used for the removal of —CH_2OH groups—*e.g.*, sodium sulfite solution is effective, although care must be taken to choose conditions such that attack by the reagent on the disulfide bond of wool is limited.

It is probable that the —CH_2OH groups can be removed by heating for a longer time than 30 min. at temperatures below 120°C. For example, it has

been stated that the polymer can be made insoluble in aqueous ethanol by heating at 85°C for 90 min., and it was assumed that some cross-linking took place [3], *e.g.*,



It has been confirmed that a surface deposit of the *N*-hydroxymethyl polymer can be rendered insoluble in aqueous ethanol by heating at 85°C for 90 min. The polymer, however, remains soluble in 90% formic acid, and it is doubtful whether cross-linking takes place to any appreciable extent by heat treatment. Nevertheless, insolubility in aqueous ethanol, and hence effectiveness in reducing felting shrinkage, can be achieved by using temperatures below 120°C.

Acknowledgments

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Frictional Properties of Jute and Some Other Long Vegetable Fibers

Part I: General Study of Characters

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Abstract

An inclined-plane apparatus has been devised for assessing the coefficient of friction of jute and allied fibers, their meshlike structures being duly considered. The nature of slip and the effects of combing, orientation of pads, normal pressure, moisture, and wax have been studied.

Introduction

Frictional forces play an important role in the drafting processes, as well as in the formation of the yarn. As Balls [2] observed, up to the drafting operations, friction contributes to irregular attenuation and hence to the production of uneven yarn; afterwards, frictional forces help in gripping the chain of fiber bundles in succession; friction also influences the minimum twist requirement for a yarn. Earlier experiments [25] on jute yarns showed an increase in strength on solvent extraction; that this was probably due to increased fiber friction has been shown in the present experiments. Friction, therefore, influences yarn strength.

The resistance offered by surface irregularities due to small sawlike transverse ridges and grooves on the walls of mature jute fiber [3], by channels along the fiber length due to polygonal cross-section of the filament, and by the meshlike structure are among the principal factors contributing to friction.

The cohesive forces of the hygroscopic constituents of the vegetable fibers may also contribute to friction, as suggested by Hardy [10] and Mercer [17] for metal and wool surfaces, respectively.

The literature on the frictional properties of long vegetable fibers is scanty. Sen and Nodder [26] devised an apparatus, similar in principle to those of Adderley [1] and other workers [21, 24], in which a jute filament is drawn by an O'Neill float between two pads pressed normally; only comparative values of "slipperiness" of single filaments from different varieties of jute were determined by it.

The "inclined-plane" [4, 20, 28, 29], the "capstan" [8, 13, 15, 16], the "Lepidometer" [7, 27], and the "stick-slip" methods [5, 9, 18, 19] have been used previously on other textile fibers. Methods based on damping of oscillations by fiber friction [12] and on the slippage of one of two twisted fibers [14] have also been tried.

Experimental

Of the methods cited above, the "inclined-plane" method was found most suitable. Although it is not very sensitive, this method has the special advantage of giving the coefficient of friction directly, without depending upon springs or torsion wires, which require frequent calibration.

Long vegetable fibers, except for a few, are meshlike in structure. Even after passing through all the stages of processing, jute filaments are not free from meshes and branches. Instead of taking observations on single filaments after removing these branches, it was decided to study the properties on clean, hand-combed fiber bundles in the form of pads containing remnants of the mesh structure.

Further, since in spinning, similar fibers slide against one another parallelwise, in line with previous work on cotton [2, 20], jute [26], and wool [8, 9, 14], the coefficient of friction of similar fibers sliding parallel to one another was taken as standard.

Method

When a body of weight W just slides over a plane surface, the coefficient of friction is given by

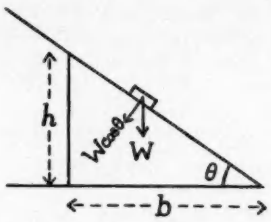

FIG. 1. *The inclined plane.*

Coulomb's formula

$$\mu = \tan \theta, \tag{1}$$

where θ is the angle which the plane makes with the horizontal.

In practice, instead of measuring θ, it is convenient to measure the vertical height, h (Figure 1), of the point of intersection of the inclined plane and a vertical line at a fixed distance, b, from the axis of rotation, $\tan \theta$ being equal to the ratio h/b. The mean coefficient of friction is then given by

$$\bar{\mu} = \frac{1}{b} \cdot \bar{h}, \tag{2}$$

where $\bar{h}$ is the mean value of the height readings.

In this method, the normal pressure per unit area, N, on the pad depends upon θ, and is given by

$$N = \frac{W \cos \theta}{A} = \frac{W}{A} \cdot \frac{1}{\sqrt{\mu^2 + 1}}, \tag{3}$$

where A is the apparent area of contact, and not the actual area of contact, which is much less than the former [6].

Apparatus

A sketch of the inclined-plane friction tester, as constructed for this work, is shown in Figure 2. The upper surface of the brass plate, AB, 6 in. × 3 in., hinged at axis X at the end of a horizontal wooden base, M, constitutes the inclined plane. The plate is thick enough so as not to sag when the heavy (380 g.) upper plate, CD, 3 in. × 3 in., is placed on it. At the zero position the lower face of AB and also the upper edge of its pointer, P, lie in the plane of the base. A transparent scale with two graduated vertical lines, V and V', at 20 cm. and 15 cm., respectively, from X, is fixed on a pillar, L; the pointer moves just behind it. The reading on a vertical line at the point of intersection with the upper edge of the pointer gives the height h.

Four brass strips with screws clamp the fiber pads at A, B, C, and D, the first two for the inclined plane and the other two for the sliding plate. Boundary marks on the strips fix the apparent area of the pads.

To operate, the inclined plane is brought to the zero position and is made horizontal by levelling screws SC. The plane, with the pads in contact, is then raised by winding a string, S, on a steel rod, R, $\frac{3}{16}$ in. in diameter and resting on the pillars, L and L′. Since the static friction depends upon the angle of inclination, and very little upon its rate of variation, the properties of the string do not affect the result significantly, and the use of a motor for uniform rotation of the plane is avoided. The rotation should, however, be slow and smooth.

As soon as a slip occurs, the handle, H, is released, and the plates are left at the position reached, for the backward motion—*i.e.*, fall under gravity—is arrested by the upper catch, K, acting on a toothed wheel, T, fitted on R. This steady state facilitates observation. The plane may be lifted further until a second slip occurs, when the plane is left at a stationary position and the reading taken. Still higher-order slips may also be obtained by continuing the process. The plane is brought to the zero position by displacing K slightly.

To obviate the personal error of rotating the plane beyond the point of slippage, particularly when slips are of small length, an automatic catch, K′, is fitted below the wheel and is worked by a battery-operated electromagnet, E. When the pads are put in contact, a metallic contact at the studs, U and U′, completes the circuit, and K′ is attracted away from the wheel, allowing the plane to rotate. As soon as a slip occurs, contact at U and U′ is broken and K′ falls back on the wheel by its own weight and stops the forward rotation automatically. The backward motion is not, however, obstructed by K′.

When required, the movement of the sliding plate can be recorded on a chart by means of a stylus fitted to the rear edge of the sliding plate. Such records are shown in Figure 4. The chart is so placed on the vertical screen, N, that the two vertical lines of the chart are at distances of 5 cm.

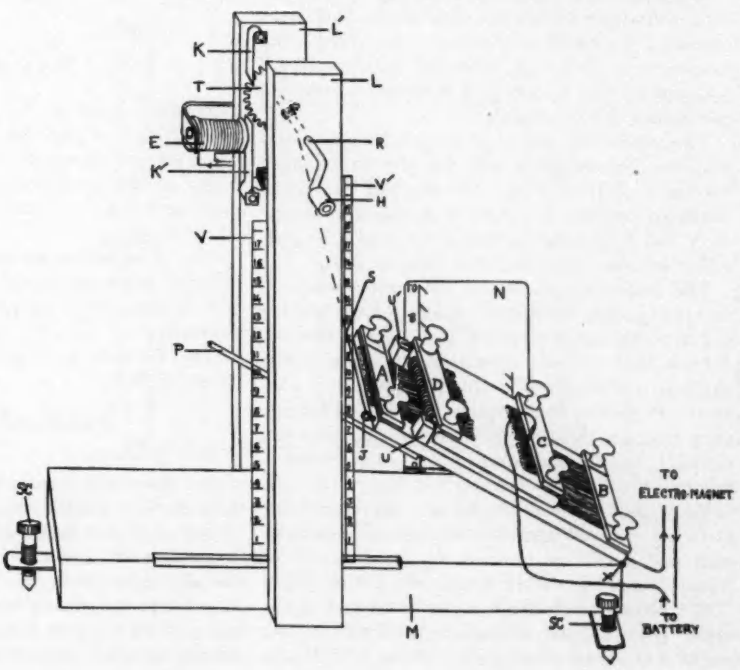

FIG. 2. *Inclined-plane friction tester.*

and 10 cm. from X, the base line of the chart lies on the base plane of the instrument, and the inclined lines of constant μ radiate from X. At the zero position, the stylus touches the bottom of the left vertical line, and as the plane is raised it describes an arc; when a slip occurs, a radial line is marked off quickly. On further rotation of the plane, arcs and radial lines repeat alternately. The chart is directly calibrated in μ, the arcs indicating increase of μ, and the radial lines indicating motion at a particular value of μ.

To study the nature of successive slips, the catch, K′, is kept off the wheel or is removed.

Procedure

A 14-in. fiber bundle, weighing approximately 250 mg. per in., from which to make the two pads required (one to attach to the inclined plane, and the other to the sliding plate), was prepared. A full-length representative sample, with barky roots removed, was cut to several 14-in. portions; the bundle was built up by collecting fiber strands from each portion after a standard combing treatment—5 drawings, both ends, on coarse gill pins (from second drawing frame) and 5 drawings, both ends, on fine gill pins (from Hessian roving frame), the last one or two of which, called the "final combing," was given at the time of pad preparation to ensure parallelism of fiber strands.

The bundle was spread uniformly, by means of a pin, over the lower plate, AB, between the boundary marks (a width of 2 in.), keeping half the length projected beyond A. After clamping the bundle at A, the final combing was given down the pad, which was then stretched and clamped at B.

The projecting portion of the bundle was cut, and the cut end was spread uniformly over a width of 2 in. on the upper plate at C and clamped thereon. After a final combing treatment, the other end of the pad was clamped at D, as illustrated in Figure 3. Projecting fiber strands, as at (e) in Figure 3, were trimmed off. Small fluffiness was, however, not likely to affect the result, as the normal pressure was high.

The upper pad was placed over the lower, end D facing A, such that the relative movement of each pad would be opposite to the direction of combing; and the electric circuit was completed.

The plane was gradually raised until just as the upper plate slipped it became stationary. The height h was read off on scale V (or on V′ if V was

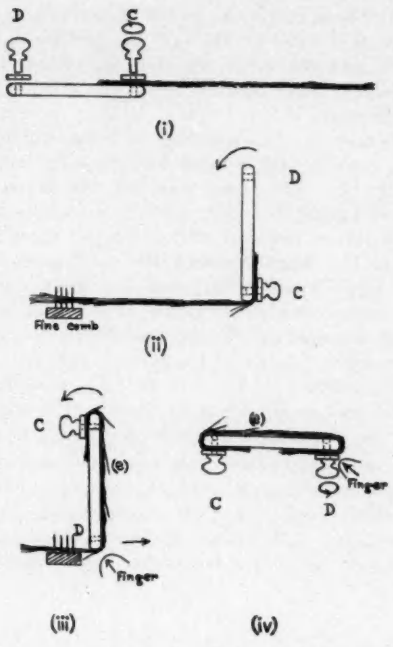

FIG. 3. *Mounting of the upper pad.*

beyond the reach of the pointer), and, from equation (2), $\tilde{\mu}$ was given by $\tilde{h}/20$ or $\tilde{h}/15$, depending upon which scale was used. The mean was usually based on 20 observations, one only for each pair of pads, and had a standard error of about 2% (Table I) of the mean.

The observations with crossed pads were taken without using the automatic catch because the circuit broke, due to creeping, before the actual slip occurred.

The bundles were conditioned and tested at 78 ± 3% R.H.

Results and Discussion

Nature of Sliding

In the series of experiments carried out with pads parallel, several typical zig-zag records of sliding, as shown in Figure 4, with alternate arcs and radial lines, were obtained. The radial lines indicate that the slips occurred in one, two, or more stages, and that increasing obstructions, due to better engagement of the pads, at higher stages were overcome by increasing the slope as indicated by the arcs.

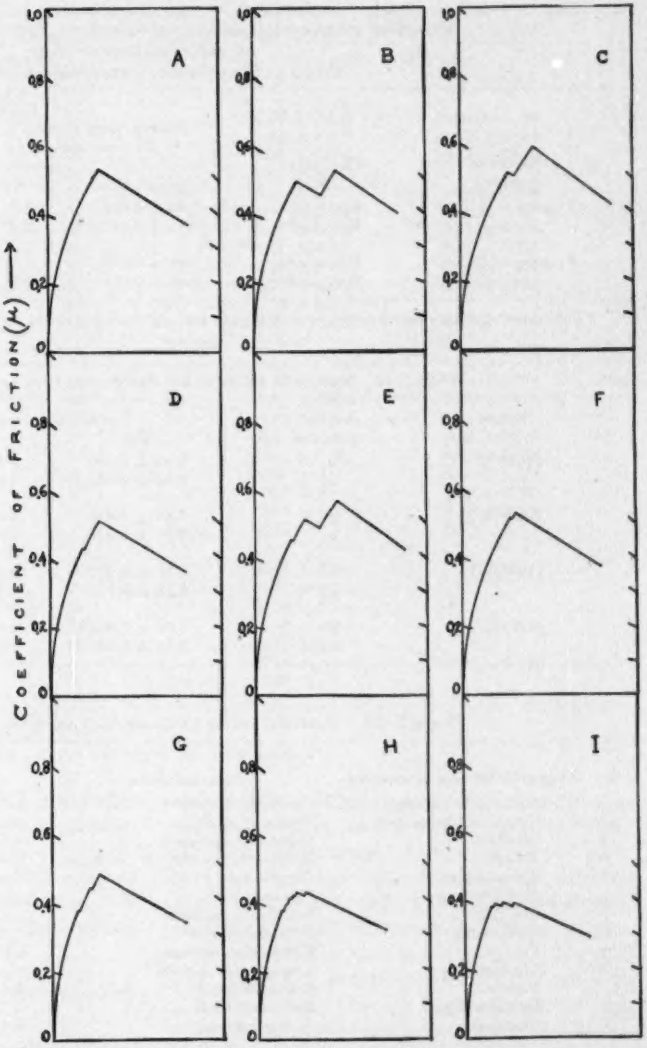

FIG. 4. *Typical records of the sliding of the upper plate.*

In some cases, more than one slip did not occur; therefore, the coefficient of friction corresponding to the first slip was always taken as standard.

The repeated slips and subsequent stickings are somewhat similar to the "stick-slips" of Bowden and Leben [5] on metal surfaces, and of Mercer [19] on wool-fiber surfaces; but here static friction, and not kinetic friction, is measured, and the pull on the slider does not diminish after a slip, so that subsequent slips corresponding only to higher values of coefficient of friction are possible.

Effect of Combing

A clean jute fiber was subjected to two experiments with different combing treatments. Table I shows that additional combing lowers the friction

TABLE I. EFFECT OF COMBING, ORIENTATION OF SLIDING FIBERS, AND REPETITION OF OBSERVATIONS ON THE SAME PAIR OF PADS
(SAMPLE: CLEAN WHITE JUTE (J1384 + 1386(W))

Nature of combing	Obs. taken on:	Coefficient of friction: Sliding fibers parallel to fixed ones — Mean (μ) ± s.e.	Fractional s.e. × 100	Sliding fibers perpendicular to fixed ones — Mean ($\mu_\perp$) ± s.e.	Fractional s.e. × 100
5 coarse + 1 fine*	Fresh pads	0.50 ± 0.011	2.2	0.45 ± 0.007	1.7
	Used pads	0.45 ± 0.011	2.3	0.40 ± 0.007	1.6
5 coarse + 10 fine	Fresh pads	0.49 ± 0.012	2.5	0.42 ± 0.006	1.5
	Used pads	0.44 ± 0.011	2.5	0.38 ± 0.005	1.3

* Five drawings, both half-lengths, on coarse pins and one drawing, in the same way, on fine pins.

TABLE II. VARIATION OF FRICTION ALONG THE LENGTH OF THE FIBER REED

Sample No.	Property measured	Position from which the sample was drawn: Top	Middle	Root
J1859	μ	0.48 ± 0.009	0.46 ± 0.007	0.50 ± 0.009
	$\mu_\perp$	0.41 ± 0.005	0.40 ± 0.006	0.45 ± 0.007
J1109(W)	μ	0.69 ± 0.015	0.68 ± 0.016	0.68 ± 0.014
	μ	0.61 ± 0.016	0.62 ± 0.014	0.61 ± 0.007
J1092(W)	μ	0.55 ± 0.012	0.57 ± 0.015	0.52 ± 0.012
	$\mu_\perp$	0.50 ± 0.013	0.50 ± 0.005	0.46 ± 0.013
J1715(W)	μ	0.46 ± 0.007	0.46 ± 0.007	0.45 ± 0.007
	$\mu_\perp$	0.39 ± 0.004	0.39 ± 0.005	0.39 ± 0.006

TABLE III. COEFFICIENTS OF FRICTION OF SOME LONG VEGETABLE FIBERS

No.	Name of the fiber as received	Botanical name	Coefficient of friction: μ ± s.e.	$\mu_\perp$ ± s.e.	Nature of slip*
1	White jute (average)	*Corchorus capsularis*	0.54	0.47	A–F
2	Tossa jute (average)	*Corchorus olitorius*	0.45	0.39	A–F
3	Meshta	*Hibiscus cannabinus*	0.50	—	A, D
4	Roselle	*Hibiscus sabdariffa*, var. *Altissima*	0.69 ± 0.009	0.58 ± 0.007	
5	*Urena lobata*	*Urena lobata*	0.60 ± 0.010	0.51 ± 0.008	C–E
6	*Helicteres isora*	*Helicteres isora*	0.58 ± 0.009	—	A, B
7	Desigogu	*Hibiscus cannabinus*	0.51 ± 0.009	0.45 ± 0.007	D–G
8	Sunn hemp	*Crotalaria juncea*	0.50 ± 0.020	0.40 ± 0.004	A–C
9	Flax	*Linum usitatissimum*	0.44 ± 0.004	0.39 ± 0.003	F–I
10	Linseed flax	*Linum usitatissimum*	0.41 ± 0.005	0.36 ± 0.006	
11	Ramie	*Boehmeria nivea*	0.61 ± 0.027	0.50 ± 0.010	A, D
12	*Sterculia villosa*	*Sterculia villosa*	0.76 ± 0.024	0.57 ± 0.014	A, D, E
13	Pineapple	*Ananas comosus*	0.62 ± 0.009	0.57 ± 0.010	A, D

* Letters refer to the curves in Figure 4.

at the first slip by a small amount when the sliding fibers are parallel to the fixed ones, and to a greater extent when the former are at right angles to the latter. It was also observed that additional combing had a greater effect on the second slips, and their frequency of occurrence was diminished.

Effect of Orientation of the Pads

Tables I and II show that when the fibers on the sliding pad are orientated at right angles to those on the fixed one, the coefficient of friction, $\mu_\perp$, is less than that, μ, obtained when the fibers are parallel, and that the variation of the readings is

TABLE IV. RELATIONSHIP BETWEEN FIBER FRICTION AND YARN PROPERTIES

Fiber No.	Yarn properties Q.R.*	Wt.C.V.(%)†		Coefficient of friction $\mu \pm$ s.e.	$\mu_\perp \pm$ s.e.
White Jute					
J1075	122	22		0.52 ± 0.005	0.48 ± 0.006
J1859	112	—		0.48 ± 0.005	0.42 ± 0.003
J1084	110	21		0.53 ± 0.008	0.47 ± 0.007
J1138	104	21		0.60 ± 0.011	
J1087	100	22		0.44 ± 0.006	0.39 ± 0.005
J1099	91	21		0.56 ± 0.012	
J1092	88	25		0.54 ± 0.010	0.47 ± 0.008
J1500	77	20		0.48 ± 0.005	0.44 ± 0.006
J 465	71	25		0.54 ± 0.011	0.45 ± 0.007
J1109	65	26		0.69 ± 0.009	0.62 ± 0.008
J1111	62	28		0.54 ± 0.009	
J 985	54	33		0.56 ± 0.007	0.52 ± 0.006
			Average	0.54	0.47
Tossa Jute					
J1770	117	25		0.42 ± 0.009	0.36 ± 0.004
J1771	111	28		0.41 ± 0.008	0.36 ± 0.006
J1749	108	22		0.42 ± 0.004	
J1704 + 1709	100	23		0.47 ± 0.008	0.40 ± 0.007
J1740	92	22		0.45 ± 0.009	0.38 ± 0.004
J 466	89	25		0.56 ± 0.005	0.43 ± 0.008
J1715	88	21		0.46 ± 0.004	0.39 ± 0.003
J1736	85	24		0.45 ± 0.009	0.39 ± 0.008
			Average	0.45	0.39
Meshta					
J2374	71	26		0.54 ± 0.013	
J2391	71	23		0.48 ± 0.012	
SR194	68	24		0.49 ± 0.016	
J2333	67	25		0.44 ± 0.010	
J2384	62	26		0.41 ± 0.009	
'X'	—	—		0.61 ± 0.015	0.53 ± 0.016
			Average	0.50	

* Q.R. (yarn-quality ratio) $= \frac{\text{Breaking load (lbs.)}}{\text{Grist (lbs./spindle)}} \times 100.$

† Wt.C.V.(%) is the coefficient of variation of the weights of 2-in. yarn pieces.

also less for the former position. This is probably due to the longitudinal repetition of irregularity waves on fiber surface.

In Table I, μ and $\mu_\perp$ were obtained from separate sets of pads, but in subsequent tables, $\mu_\perp$ was obtained from the same pair of pads after finding μ and hence was a little underestimated.

Effect of Repetition of Observations on the Same Pair of Pads

Table I shows that when observations are repeated on the same pair of pads, μ is lowered by about 10%. This is due, probably, to polishing of pad surfaces during the first observation.

Variation of Friction Along the Length of the Fiber Reeds

Measurements were made at "top," "middle," and "root" portions of bundles of four full-length jute samples of different qualities and species; the results are given in Table II. The "middle" sample was prepared by cutting around the center of gravity of the whole bundle, as determined by a special balance [22], and the other two samples were determined in the same way from the remaining portions.

The results show that if the pads are free from bark, there is a small variation in the values of coefficients of friction at "top," "middle," and "root" portions, but without any definite order.

Coefficients of Friction of Some Long Vegetable Fibers

The coefficients of friction of several White and Tossa jute fibers and eleven other long fibers, some of which are jute substitutes, were compared. The results are given in Table III. For jute and Meshta, only average values of the figures given in Table IV have been incorporated into Table III.

The average coefficient of friction of Tossa jute appears to be lower than that of White jute; within the same variety of either, the variation of the coefficient is less. For Meshta, the values vary considerably from sample to sample. Flax has the same order of friction as Tossa jute, while Sunn hemp, Desigogu, and *Helicteres isora* samples are comparable with White jute in this respect. *Urena lobata* and Roselle have still higher values. It is therefore likely that a lower twist may be sufficient to spin these fibers by the jute process.

The nature of slip was also observed for most of the fibers. The letters in the last column of Table III indicate the respective curves in Figure 4 to which the slips corresponded. For flax, some observations were peculiar, the sliding pad passing through several "stick-slips" at short intervals before the final slip.

The values of coefficients of complexity given by Sen and Nodder [26] show that Tossa jute is not as meshlike as White jute; this, probably, is one of the causes of the low friction of the former. The low friction of flax fiber may be due to its cells being cylindrical and round-edged and to its high wax content, the peculiar nature of its slips being attributed to the frequent occurrence of dislocations or transversely extending nodes.

Relationship Between Fiber Friction and Yarn Properties

Several White jute, Tossa jute, and Meshta fibers of known yarn properties were examined for friction. The results are given in Table IV.

For jute, no close relationship appears to exist between the coefficients of fiber friction and yarn-quality ratio or weight coefficient of variation (%), although the results show a tendency for jute fibers producing low-quality yarn to have a high coefficient of friction; for Meshta, the relationship seems to be closer, but the tendency is opposite to that for jute.

The lack of correlation is probably due to the combined action of two opposite effects of fiber friction on the yarn produced: friction helps to maintain the structure and, hence, the strength of the yarn; on the other hand, a higher friction is likely to cause irregularity in structure and, hence, the diminution of yarn strength. For jute, both of the effects seem to balance each other; for Meshta, the former effect appears to be slightly predominant.

Effect of Variation of Normal Pressure

In order to see if Amonton's law of independence of the coefficient of friction and the variation of normal pressure applies in the case of long vegetable fibers, a few experiments were made with two samples of clean jute at different normal pressures. For high normal pressures, extra loads in the form of brass plates were placed on the upper plate; for low pressure, a wooden replica of the upper plate was used.

The normal pressure, N, was calculated from equation (3). The area (approximately 6 sq. in.) of the upper plate covered by fiber was taken as the apparent area of contact, A. The normal pressure would give an indication of the condition of the pad fiber at the time of experiment.

The results, as plotted in Figure 5, show that at low pressures, the coefficient of friction decreases appreciably with increase of pressure; at high pressures (above 15 g./cm.^{2} in this case), it becomes practically independent of pressure.

When the fibers of one pad are parallel to those of the other, within a short range of pressure (3 to 30 g./cm.^{2}) the approximate μ-N curves ((a) and (b) in Figure 5) obtained are of the rectangular hyperbolic type, as obtained by Martin and Mittelmann [16] and by Mercer and Makinson [19] in the case of wool fibers, having an equation of the form

$$\mu = \frac{a}{N} + b, \tag{4}$$

where a and b are positive constants. From this equation, the frictional force, F, is given by

$$F = \mu N = a + bN. \tag{5}$$

These results are similar to those of Gralén [9, 14] for wool, of Morrow [20] for cotton, and of Hardy [11] for lubricated plane metal surfaces.

In line with the results of other workers, the existence of the term a can be explained by assuming the existence of some extratangential forces on the surfaces of contact in the form of molecular attraction between the surfaces or in the form of resistance due to interlocking between the crests and the troughs of the two surfaces, as is likely to exist even when $N = 0$.

A similar effect was obtained when the fibers in two pads were placed across one another. The pair of pads used for the parallel-slippage experiments were used here. The apparent area of con-

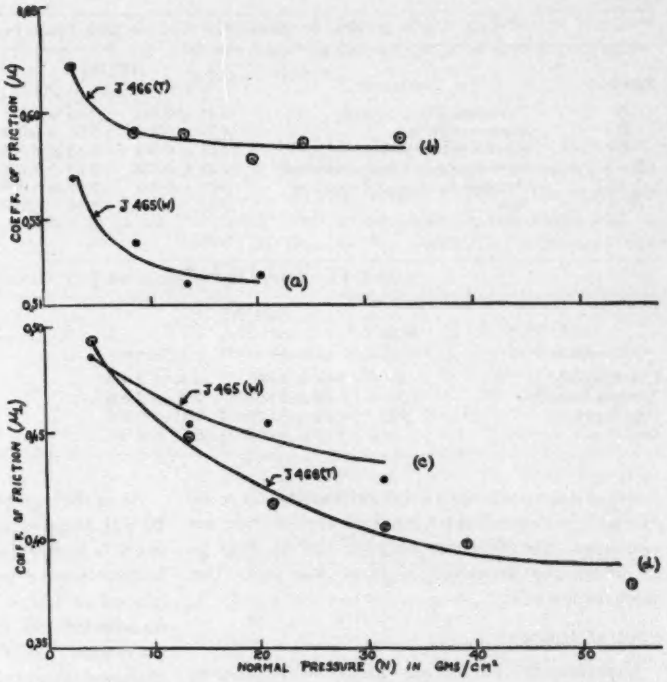

FIG. 5. *Effect of normal pressure on fiber (jute) friction.*

tact was only about 4 sq. in. in this case. The results are plotted in Figure 5 ((c) and (d)). The curves deviate largely from equation (4), and show that although μ_1 diminishes with increase of pressure, the critical point above which the effect of pressure is negligibly small is much higher in the pressure scale than when the fibers are parallel.

Effect of Wax

Vegetable fibers invariably contain some fats and waxes (and since most of these are easily extractable without damage to the fiber, it is likely that they are present largely on the surface). It would therefore be of interest to determine their effects on the friction of the fiber. One set of experiments was carried out using two jute fibers—one Tossa and the other White—after removal of fat and wax, and another set was carried out after deposition of some paraffin wax on the fibers.

In the first experiments, the bundles prepared after preliminary combing were subjected to extraction in a Soxhlet apparatus with a mixture of alcohol and benzene (1:1) for 8 hrs. The dewaxed fiber was conditioned further for 3 days, and was then subjected to the final combing. The coefficient of friction was then measured.

In the second experiments, after preliminary combing the bundles prepared from raw jute were heated for 3 hrs. at 105°C and were then immediately immersed in a 5% solution of paraffin wax (B.D.H.) in benzene and shaken for about an hour. The bundles were then taken out of the solution and conditioned. Benzene gradually evaporated off, leaving a film of solid paraffin wax on the surface of the fiber strands, the weight of the paraffin film being about 4% of the weight of air-dry jute. After usual conditioning and final combing, the bundles were tested for friction.

The results given in Table V show that removal of fat and wax increases friction to a large extent, while deposition of solid wax diminishes it. Apart from forming a layer on the surface, wax possibly fills up some of the depressions as well.

The last 3 rows of Table V show that though the

TABLE V. EFFECT OF WAX ON JUTE FIBER FRICTION

Row No.	Treatment	J465(W) $\mu \pm$ s.e.	J465(W) $\mu_\perp \pm$ s.e.	J466(T) $\mu \pm$ s.e.	J466(T) $\mu_\perp \pm$ s.e.
A	Untreated	0.54 ± 0.011	0.45 ± 0.007	0.56 ± 0.005	0.43 ± 0.008
B	Solvent-extracted	0.79 ± 0.021	0.65 ± 0.018	0.73 ± 0.010	0.59 ± 0.012
C	Paraffin wax deposited	0.46 ± 0.004	0.38 ± 0.005	0.44 ± 0.004	0.36 ± 0.003
B−A	Increase due to solvent extraction	0.25 ± 0.024	0.20 ± 0.019	0.17 ± 0.011	0.16 ± 0.014
A−C	Decrease due to wax deposition	0.08 ± 0.012	0.07 ± 0.009	0.12 ± 0.006	0.07 ± 0.009
B−C	Sum	0.33	0.27	0.29	0.23

TABLE VI. EFFECT OF MOISTURE ON JUTE FIBER FRICTION

Condition	J465(W) R.H. (%)	J465(W) $\mu \pm$ s.e.	J465(W) $\mu_\perp \pm$ s.e.	J466(T) R.H. (%)	J466(T) $\mu \pm$ s.e.	J466(T) $\mu_\perp \pm$ s.e.
Low humidity	46	0.41 ± 0.008	0.34 ± 0.005	43	0.37 ± 0.006	0.34 ± 0.004
Medium humidity	58	0.46 ± 0.004	0.40 ± 0.004	62	0.48 ± 0.007	0.41 ± 0.008
High humidity	78	0.54 ± 0.011	0.45 ± 0.007	80	0.56 ± 0.005	0.43 ± 0.008
Wet		1.09 ± 0.009	0.72 ± 0.008		1.07 ± 0.006	0.71 ± 0.004

increase due to solvent extraction and the decrease due to wax deposition on raw jute are different for two jutes; the difference between the frictions of extracted and deposited fibers is practically the same for both.

Effect of Moisture

Experiments were carried out on one White and one Tossa jute at three relative humidities (within 40% to 80%). The bundles prepared after preliminary combing were conditioned for more than 7 days—one set in a room conditioned at 78 ± 3% R.H., and two other sets in desiccators containing solutions of calcium chloride corresponding to 60% and 45% R.H. After conditioning, friction experiments were carried out within ±5% of the conditioning humidities; after each reading, the relative humidity was recorded. The means of these R.H. readings and the corresponding mean coefficients of friction are given in Table VI and are plotted in Figure 6.

In order to determine the effects of a still higher moisture content, another set of experiments was carried out on fibers in a soaking-wet condition. Each bundle prepared after preliminary combing was soaked in tap water for 1 min. and was then squeezed by hand so that it retained about twice its dry weight of water. The final combing was given to the bundle, and the friction measured immediately. These results are included in Table VI.

As in the case of other textile materials [8, 13, 17, 20, 23], the results show that friction between jute fibers is highly dependent upon relative humidity, friction always increasing with the rise of R.H.; control of humidity is therefore essential in the measurement of coefficient of friction. When the fibers slide parallel to each other, the μ-R.H. curves (Figure 6 (a) and (b)) are approximately linear, with a slight concavity towards the R.H. axis, within the range of humidities studied. The approximate rate of increase of coefficient of friction per 1% rise of R.H. was about 0.004 for sample J465(W), and 0.005 for sample J466(T). The large increase of friction on wetting indicates that the trend of rise of μ with R.H. continues beyond 80% R.H.

When the fibers slide at right angles to each other, the curves (Figure 6 (c) and (d)) deviate largely from linearity and the concavity towards the R.H. axis is pronounced. It should be noted that these observations were taken on the pads used in the parallel-slip experiments.

The rise of friction with relative humidity supports the view that the molecular forces of the adsorbed moisture between two jute surfaces add to the simple Coulombian friction.

Summary and Conclusions

1. An inclined-plane apparatus suitable for long fibers and its working procedure have been described.

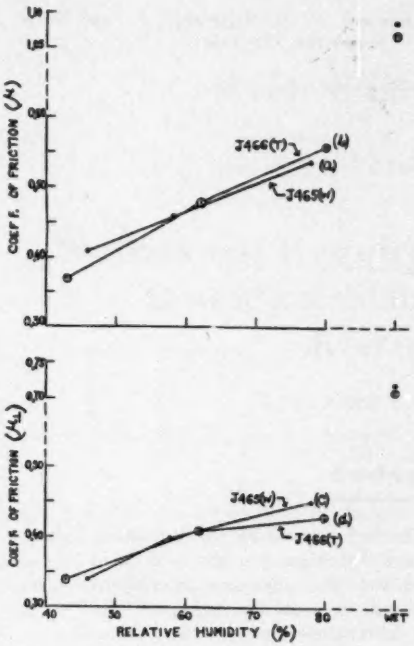

FIG. 6. *Effect of relative humidity on fiber (jute) friction.*

2. The nature of slip is found to vary from fiber to fiber, sliding often taking place by "stick-slips," with increase of inclination.

3. Increased combing reduces friction only to a small extent.

4. Friction is less when the fibers slide perpendicular to each other than when they are parallel.

5. μ obtained from a used pair of pads is less than that obtained from a fresh pair.

6. μ varies slightly along the length of jute fiber reeds, but without any definite order between the "top," "middle," and "root" portions.

7. μ decreases with increase of normal pressure, but at high pressures (above 15 g./cm.^{2}) it is practically independent of pressure.

8. Removal of natural fat and wax increases μ of jute, and deposition of paraffin wax diminishes it.

9. Jute friction is rather sensitive to moisture, μ rising with the relative humidity.

10. Friction of Tossa jute is less than that of White jute; friction of flax and Tossa jute are of the same order.

11. There is only a slight tendency of the jute fibers producing weaker yarns to have higher coefficients of friction.

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Earl K. Fischer

Earl K. Fischer, Chief of the Organic Coatings Section of the Bureau of Standards, Washington, D. C., died of a heart attack on August 3. Born in Milwaukee, Wisconsin, Dr. Fischer graduated from the University of Southern California in 1927, and received his Ph.D. degree from the University of Wisconsin in 1931. For three years he held a Stieglitz fellowship in physical chemistry at the University of Chicago. An expert in the field of surface and colloid chemistry, and on paints, varnishes, and other protective coatings, Dr. Fischer for six years was head of the Interchemical Corporation's physical chemistry laboratory. Before joining the Bureau in 1949, he headed the physical chemistry division of the Institute of Textile Technology, in which position he became familiar with textile problems.

Dr. Fischer's interests were broadly diversified. He was a member of a number of scientific societies, including the American Chemical Society, the American Institute of Physics, and The Fiber Society. He published many technical papers, and was the author of a recently published book, "Colloidal Dispersions." He was a member of the board of Associate Editors of TEXTILE RESEARCH JOURNAL. As a member of the Publications Committee of Textile Research Institute in 1945, he assisted in shaping the editorial policies of the JOURNAL in its changeover from TEXTILE RESEARCH, previously published by the Institute and The Textile Foundation.

INDUSTRIAL SECTION

Nutritional Requirements During Aerobic Biological Stabilization of Cotton Kiering Waste*

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Contribution from the Sedgwick Memorial Laboratories, Massachusetts Institute of Technology, Cambridge, Massachusetts

WASTE KIERING LIQUOR from the detergent ing of cotton is one of the most objectionable wastes from cotton mills from the standpoint of volume and strength. Consequently, its treatment prior to disposal is often a problem of some importance. The treatment of textile wastes is usually accomplished at a municipal plant in combination with domestic sewage or in a mill-operated disposal plant by equalization and chemical precipitation [1]. Treatment in a municipal plant is often the most economical method, but municipal officials are frequently reluctant to accept kiering waste and other strong textile wastes in fear of upsetting biological treatment processes. Textile manufacturers are aware of the economic implications of movements to exclude their wastes, and have been active in the investigation of methods by which textile wastes can be treated successfully in conjunction with domestic sewage [2, 3].

Because cotton kiering and many other textile processes are batch operations, the resulting erratic nature of the waste discharge is an important reason for difficulties encountered in biological treatment. Equalization of flow by using holding tanks is a means for solving this problem. Another basic source of difficulty is that some textile wastes are deficient in certain nutritional substances that are essential for the satisfactory functioning of biological processes. To meet this problem, the waste having a deficiency may be treated in combination with a waste that contains an excess of nutrients, such as domestic sewage, or supplementary nutrients in some form may be added to accomplish rapid and economic stabilization.

Several investigators have reported that the treatment of kiering and other textile wastes by using biological methods is successful when the waste is mixed with a sufficiently large volume of domestic sewage [5, 8, 9]. The North Buffalo activated sludge plant at Greensboro, N. C., was started in operation with domestic sewage only. Later, when textile wastes, including kiering waste, were added to the extent of about 15% to 20% of the mixture, the results were a deterioration in quality of the return sludge and a sludge cake that was difficult to handle by vacuum filtration. These problems were met by resorting to reaeration of return sludge and an increase in the amount of sludge conditioner used [1, 7].

Objectives and Scope of Work

The purpose of the laboratory studies with which this paper is primarily concerned was to determine the nitrogen and phosphorus requirements during the biological stabilization of cotton kiering waste in order to provide a sound basis for proportioning of flow to municipal plants or the addition of supplementary nutrients at industry-owned treatment

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TABLE I. COTTON KIERING WASTE AND DOMESTIC SEWAGE ANALYSES

Factor	Run C		Run E	
	Cotton kiering	Domestic sewage*	Cotton kiering	Domestic sewage*
5-day B.O.D. (p.p.m.)	2510	196	2745	193
Total nitrogen (p.p.m.)	98	26.1	97	26.0
Organic nitrogen (p.p.m.)	96	12.6	85	12.0
Total phosphorus (p.p.m.)	20.8	3.97	15.6	4.96
Soluble phosphorus (p.p.m.)	11.45	2.55	—	3.25
pH	12.2	—	12+	—
B.O.D./total N	26	7.5	28	7.4
B.O.D./total P	121	49	176	39

* Average values.

plants. The effects of nutritional deficiencies on process efficiency were also studied.

Two aerobic methods of biological treatment are ordinarily used for stabilizing the more dilute organic wastes—namely, trickling filters and the activated-sludge process. Experimentation on a laboratory scale with trickling filters is quite costly and difficult; on the other hand, experimental studies with activated sludge are easily conducted.

Numerous studies by various investigators have shown that a great similarity exists between the biological nature and action of trickling-filter slimes and activated sludge. Therefore, it was decided to make the basic nutritional studies using the activated-sludge process. A few correlation studies were made with laboratory-scale trickling filters to test the validity of applying the data obtained by means of activated sludge to trickling-filter operation.

Two conditions of treatment were recognized, and experimental procedures were adopted for the study of both:

1. The treatment of industrial waste and domestic sewage in mixtures such as might be encountered in a municipal treatment plant. The question is, what quantities of waste can be tolerated in the mixture being treated?

2. The treatment of industrial wastes without benefit of admixture with a large amount of sewage, as in the case of a private industrial-waste treatment plant. Because only a fraction of the required nutritional elements were available under these conditions, supplementary nutritional elements were added in varying amounts in order to determine the critical amounts of nitrogen and phosphorus required for rapid, satisfactory treatment.

Cotton Kiering Waste

The kiering waste used in these studies was obtained from the processing of cotton gray goods with a detergent mixture of the following approximate composition: caustic alkali (NaOH), 1%; commercial detergent, 0.25%; some silicates; and some phosphates.

About 8% to 10% by weight of the gray goods is lost in the kiering process; the resulting kiering waste contains natural sugars, starches, waxes, resins, oils, and boll fragments of the cotton, plus any artificially added sizing materials, and the original detergents. Because of the predominance of sugars and starches in the waste liquor, it is deficient in nitrogen, as indicated by a high B.O.D.-to-nitrogen ratio of about 27:1.

Sufficient waste to last an entire experimental run was obtained at one time in order to eliminate variations in waste characteristics. Analyses of the wastes used in both runs are shown in Table I. The pH was adjusted in the range 7.0 to 7.5 with concentrated sulfuric acid before use. Subsequent studies have shown that there is no need to lower the pH below 10, if at all.

Experimental Method

Apparatus

The apparatus used in the activated-sludge studies is shown in Figure 1. The equipment consists of five constant-temperature (±0.5°C) water baths, each bath containing four Pyrex glass tubes of 2.5 l. capacity. Three of the water baths were used in these studies. Air was supplied in excess to the bottom of each tube through a carborundum diffuser.

Feeding Procedure and Analytical Control

In preparation for a run, the first step was to develop activated sludge in the aeration tubes by

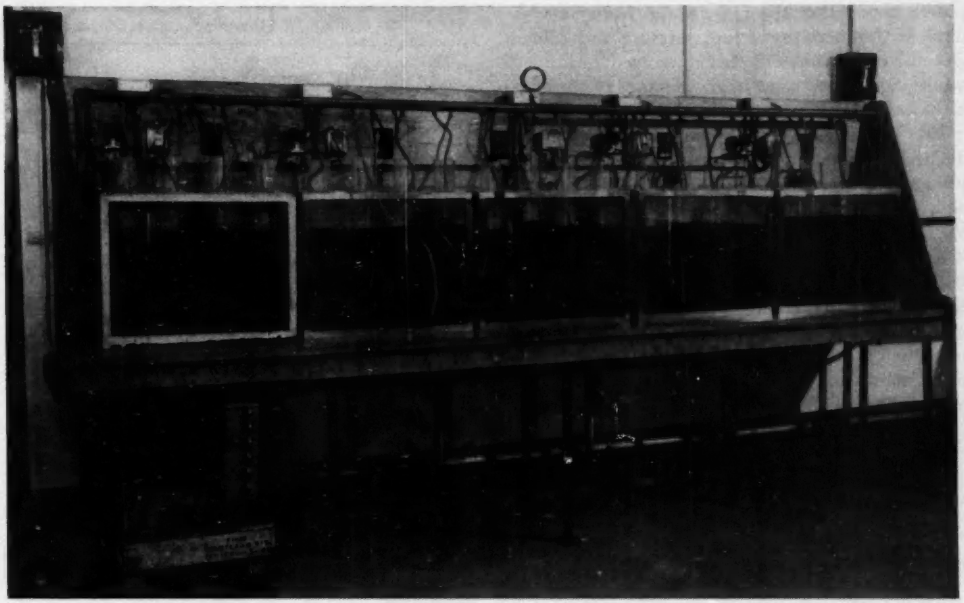

FIG. 1. *Apparatus used in activated sludge studies.*

feeding different feed mixtures. Feedings were conducted at 8-hr. intervals, and the concentrations of aeration solids were controlled at 1500 p.p.m. by wasting measured amounts of sludge at the end of each aeration period. Experiments were carried out at constant temperatures of 10°, 20°, and 30°C, to correspond to winter, spring and fall, and summer operating conditions.

After the aeration solids had built up to 1500 p.p.m., several days were allowed for acclimatization, as indicated by a consistent rate of sludge growth and effluent analysis, before the run proper was started. Acclimatization is deemed to be of utmost importance if reproducible results are to be obtained.

During the run proper, 3-day composite samples of the effluents were analyzed for various forms of nitrogen and phosphorus, and an accurate record of sludge growth was maintained. The 5-day, 20°C B.O.D.'s of all effluents were also determined on freshly collected samples several times during the course of a run. At the conclusion of a run, the remaining sludges were dried and analyzed for nitrogen, phosphorus, and volatile matter.

Analysis of Data

Experimental data were analyzed using a theoretical nutritional-balance equation based on the assumptions of treatment-process equilibrium and no net gain or loss of nutrients as a gas. In other words, the amount of nutritional element coming out of the process must be equal to the amount of nutritional element put in, or

$$I = E + \frac{Gn}{200}, \qquad (1)$$

in which I is the p.p.m. of nutrient element in the influent feed mixture; E is the p.p.m. of nutrient element in the effluent; G is the p.p.m. per day rate of sludge growth; and n is the percentage of nutrient element in the dry sludge (N is used for percentage of nitrogen, P for percentage of phosphorus). As written, the constants of equation (1) apply to the experimental conditions of three feedings per day and a 2:1 ratio of influent feed mixture to return sludge.

The term $Gn/200$, or, equivalently, $I - E$, represents the nutritional requirement of the activated sludge. Thus, nutritional requirements can be com-

puted from either the growth and sludge-analysis data or the analyses of feed mixture and effluent. Because of the inherent check involved, both methods of calculation were used. Details of the calculation method have been discussed previously [4].

The "nitrogen (or phosphorus) requirement" is defined as the amount of nitrogen (or phosphorus) utilized by the activated sludge in the stabilization of a substrate. The "maximum requirement" is the amount utilized when an excess of the nutrient is available in the feed mixture, and the "critical requirement" is defined as the amount of nutrient that must be available for satisfactory treatment plant operation. Of course, the term "satisfactory treatment" must first be defined for individual plant conditions in order to determine critical requirements.

Results—Run C: Treatment in Combination with Domestic Sewage

The combinations of kiering waste and domestic sewage used in run C are shown in Table II. No supplementary nutrients were added. The domestic sewage was obtained fresh every other day from the Boston Ward Street pumping station and refrigerated until used.

Nitrogen and Phosphorus Contents of Effluents

Average inorganic and organic nitrogen contents of the effluents are shown in Table III. As the percentage of waste in the feed mixture was increased, the inorganic nitrogen residuals of the effluents decreased markedly. This trend indicates that the excess nitrogen from the sewage was utilized in the stabilization of the cotton kiering waste. The very low residuals from the 20% waste mixtures were considered to be indicative of a nitrogen deficiency.

Residuals of organic nitrogen are in sharp contrast to the inorganic nitrogen residuals. The residual organic nitrogen increased with increasing waste load. This observation may be accounted for by the fact that the kiering waste was high in organic nitrogen, and indicates that all of this nitrogen was not in a form available to the activated sludge.

Temperature did not have very much effect on the amount of effluent inorganic nitrogen. Temperature did determine the chemical form of the nitrogen, however; nitrification occurred at 20° and 30°C but not at 10°C, and assimilation of organic forms decreased with decrease in temperature.

TABLE II. EXPERIMENTAL CONDITIONS

Tube No.	Temp. (°C)	Kiering waste (%)	Domestic sewage (%)	Supp. N (p.p.m.)	B.O.D. loading (lbs./1000 cu. ft./day)
			*Run C**		
1	*	0	100	0	24.5
2	*	5	95	0	39.0
3	*	10	90	0	53.4
4	*	20	80	0	82.5
			Run E†		
1A	10	10	5	0	35.6
2		10	5	2	35.6
3		10	5	4	35.6
4		10	5	6	35.6
1B	20	20	5	0	70.0
2		20	5	5	70.0
3		20	5	10	70.0
4		20	5	15	70.0
1C	30	20	5	0	70.0
2		20	5	3	70.0
3		20	5	6	70.0
4		20	5	9	70.0

* In run C, experiments were conducted under the same loading conditions at 10°, 20°, and 30°C.

† In run E, % waste plus % sewage plus % tap water equals 100%.

TABLE III. NITROGEN CONTENT (P.P.M.) OF EFFLUENTS—RUN C

Waste (%)	B.O.D. loading (lbs./1000 cu. ft./day)	Inorganic 10°C	Inorganic 20°C	Inorganic 30°C	Organic 10°C	Organic 20°C	Organic 30°C
0	24.5	14.2	17.5	17.0	3.5	3.6	2.9
5	39.0	7.7	8.7	7.4	6.7	6.3	4.0
10	53.4	2.2	2.6	2.3	10.7	8.6	5.3
20	82.5	0.3*	0.3*	0.4*	19.3	12.4	9.2

* Considered as indicating a nitrogen deficiency.

Average phosphorus contents of the effluents are given in Table IV. The soluble phosphorus residuals decreased as the percentage of waste was increased to 10%, but effluent phosphorus increased when the waste percentage was increased further to 20%. Evidently the nitrogen deficiency became critical before a phosphorus deficiency was reached.

Maximum Nitrogen and Phosphorus Requirements

Nitrogen requirements for the waste-sewage mixtures are shown in Table V. Requirements based on sludge analyses are in fairly good agreement with

TABLE IV. PHOSPHORUS CONTENT (P.P.M.) OF EFFLUENTS —RUN C

Waste (%)	B.O.D. loading (lbs./1000 cu. ft./day)	Soluble 10°C	Soluble 20°C	Soluble 30°C	Total 10°C	Total 20°C	Total 30°C
0	24.5	1.38	1.55	1.71	1.60	1.82	2.00
5	39.0	1.14	0.89	1.10	1.43	1.19	1.59
10	53.4	1.02	0.64	0.63	1.32	0.94	1.06
20	82.5	1.78	0.83	0.78	2.50	1.22	1.05

TABLE V. NITROGEN REQUIREMENTS FOR STABILIZATION OF COTTON KIERING WASTE—RUN C

Waste (%)	Temp. (°C)	Nitrogen requirements (B.O.D./N)* Sludge basis	Nitrogen requirements (B.O.D./N)* $I_n - E_n$ basis	Max. nitrogen requirements (best or ave. values) B.O.D./N*	Max. nitrogen requirements (best or ave. values) lbs. N/100 lbs. B.O.D. removed†
5	10	18.0	16.1	18	5.6
10		17.9	17.5		
20		<23.4‡	<29.1‡		
5	20	15.2	11.7[a]	16	6.2
10		16.4	13.9		
20		20.5‡	19.6‡		
5	30	16.1	9.8[a]	16	6.2
10		16.3	12.2		
20		16.3‡	19.1‡		

* Ratio of B.O.D. reduction of waste to nitrogen utilized by sludge growth attributed to stabilization of the waste.

† Pounds of nitrogen required per 100 lbs. of waste B.O.D. stabilized.

‡ Denotes nitrogen deficiency. See Table III.

[a] High nitrates in effluent.

those based on effluent analyses. Requirements based on sludge growth are believed to be the more reliable since the 20° and 30°C effluents contained appreciable nitrate nitrogen, and the analytical method used to determine nitrates was not considered to be very accurate.

Maximum nitrogen requirements were based on results from the mixtures that did not develop nitrogen deficiencies. Maximum nitrogen requirements were 5.6, 6.2, and 6.2 lbs. per 100 lbs. B.O.D. removed at temperatures of 10°, 20°, and 30°C, respectively.

Table VI shows phosphorus requirements based on influent-effluent analyses. The high B.O.D./P ratios for the 20% waste mixtures are believed to be the result of nitrogen rather than phosphorus deficiencies. Based on mixtures not resulting in nitrogen deficiencies, maximum phosphorus requirements were 1.0, 1.2, and 1.1 lbs. per 100 lbs. B.O.D. removed at temperatures of 10°, 20°, and 30°C, respectively.

TABLE VI. PHOSPHORUS REQUIREMENTS FOR STABILIZATION OF COTTON KIERING WASTE—RUN C

Waste (%)	Temp. (°C)	Phosphorus requirements (B.O.D./P)* $I_p - E_p$ basis	Max. phosphorus requirements (best or ave. values) B.O.D./P*	Max. phosphorus requirements (best or ave. values) lbs. P/100 lbs. B.O.D. removed†
5	10	104	102	0.98
10		101		
20		<141‡		
5	20	78	83	1.20
10		88		
20		106‡		
5	30	92	90	1.11
10		87		
20		103‡		

* Ratio of B.O.D. reduction of waste to phosphorus utilized by sludge growth attributed to stabilization of the waste.

† Pounds of phosphorus required per 100 lbs. of waste B.O.D. stabilized.

‡ Denotes nitrogen deficiency.

TABLE VII. PROCESS EFFICIENCY AND ACTIVATED-SLUDGE ANALYSES—RUN C

Waste (%)	Temp. (°C)	B.O.D. (p.p.m.) Infl.	B.O.D. (p.p.m.) Effl.	Sludge growth (p.p.m./day)	Sludge analyses S.V.I.†	Sludge analyses N (%)	Sludge analyses P (%)	Sludge analyses V_m (%)‡
0	10	196	13	198	67	6.78	1.40	76
5		312	21	318	62	8.13	1.24	83
10		427	38	440	59	8.38	1.15	86
20*		660	>100	615	68	7.48	1.24	86
0	20	196	15	198	56	7.42	1.53	82
5		312	17	384	51	7.82	1.37	84
10		427	18	536	47	8.05	1.24	87
20*		660	47	792	48	7.22	1.12	89
0	30	196	8	202	68	7.15	1.52	81
5		312	9	378	74	7.69	1.39	84
10		427	11	540	69	8.02	1.39	85
20*		660	24	950	84	7.48	1.15	87

* Nitrogen deficiency.

† Sludge volume index (Mohlman).

‡ Volatile matter.

Nutrition and Process Efficiency

The results of increasing the percentage waste in the waste-sewage mixtures on the activated-sludge process are indicated by the data in Table VII. All B.O.D. reductions were in excess of 90% with the exception of the 20% waste mixture at 10°C. Supplementary studies showed that this high effluent B.O.D. was the result of the low stabilization temperature and not the nitrogen deficiency.

All sludges had good settling characteristics, as indicated by low sludge volume indices. Increased percentages of kiering waste resulted in an increase in the nitrogen and volatile-matter contents of the sludges to the point where a nitrogen deficiency developed. A nitrogen deficiency caused a decrease in the sludge nitrogen content.

The most marked effect of increasing the amount of waste load was the increase in the rate of sludge growth. The relationship is shown in Figure 2. At a given temperature, the rate of sludge growth was directly proportional to the B.O.D. reduction of the feed mixture. This relationship held as long as a nutritional deficiency did not develop.

Results—Run E: Treatment with Addition of Supplementary Nitrogen

Run E was designed to simulate conditions that might be encountered in an industry-owned and -operated textile waste-treatment plant. Since such a treatment plant would have only a relatively small amount of sanitary sewage available, nutritional requirements of the activated sludge would have to be supplied by supplementation. Supplementary nitrogen was added in the form of ammonium sulfate, but no phosphorus was added in light of the results of run C. The waste was diluted with tap water to reduce the loading on the treatment process. Compositions of the feed mixtures used in run E are shown in Table II.

Nitrogen and Phosphorus Contents of Effluents

Average inorganic nitrogen residuals of all effluents were less than 0.7 p.p.m. These low residuals, together with the fact that many composite samples contained no detectable inorganic nitrogen, indicate that a nitrogen deficiency existed in all cases. Of course, the magnitude of the deficiency varied, depending upon the amount of supplementation. Organic nitrogen residuals existed in all effluents, with the average values ranging from 5.6 to 8.8 p.p.m.

Soluble phosphorus residuals were considerably lower in run E than in run C. The highest average residual was 0.75, and the lowest 0.22 p.p.m. The effluent phosphorus contents were highest for the mixtures that did not receive supplementary nitrogen, and lowest for those that did. Even though the phosphorus residuals were quite low, nearly constant phosphorus requirements and sludge phosphorus contents for all effluents seem to indicate that a phosphorus deficiency did not exist. (See Tables IX and X.)

TABLE VIII. NITROGEN REQUIREMENTS FOR STABILIZATION OF COTTON KIERING WASTE—RUN E*

Waste (%)	Supp. N (p.p.m.)	Temp. (°C)	Nitrogen requirements (lbs./100 lbs. B.O.D. removed)† Sludge basis	$I_n - E_n$ basis	Max. N requirements (lbs./100 bs. B.O.D. removed)† (Run C)
10	0	10	1.9	2.0	
10	2		2.6	2.5	
10	4		2.7	3.3	
10	6		3.3	3.6	5.6
20	0	20	2.3	2.5	
20	5		3.2	3.5	
20	10		3.6	4.3	
20	15		5.5	5.0	6.2
20	0	30	2.3	2.3	
20	3		2.5	2.8	
20	6		3.0	3.5	
20	9		3.7	4.2	6.2

* Nitrogen deficiency existed in all cases.

† Pounds of nitrogen required per 100 lbs. of waste B.O.D. stabilized.

TABLE IX. PHOSPHORUS REQUIREMENTS FOR STABILIZATION OF COTTON KIERING WASTE—RUN E

Waste (%)	Supp. N (p.p.m.)	Temp. (°C)	Phosphorus requirements (lbs./100 lbs. B.O.D. removed)* Sludge basis	$I_p - E_p$ basis	Max. P requirements (lbs./100 lbs. B.O.D. removed)* (Run C)
10	0	10	0.30	0.31	
10	2		0.33	0.44	
10	4		0.32	0.44	
10	6		0.33	0.44	
			0.32 Ave.	0.41 Ave.	0.98
20	0	20	0.41	0.44	
20	5		0.50	0.53	
20	10		0.46	0.54	
20	15		0.63	0.54	
			0.50 Ave.	0.51 Ave.	1.20
20	0	30	0.38	0.43	
20	3		0.39	0.44	
20	6		0.42	0.50	
20	9		0.42	0.54	
			0.40 Ave.	0.48 Ave.	1.11

* Pounds of phosphorus required per 100 lbs. of waste B.O.D. stabilized.

TABLE X. PROCESS EFFICIENCY AND ACTIVATED-SLUDGE ANALYSES—RUN E*

Supp. N (p.p.m.)	Temp. (°C)	B.O.D. (p.p.m.) Infl.	B.O.D. (p.p.m.) Effl.	Sludge growth (p.p.m./day)	S.V.I.†	Sludge analyses N (%)	P (%)	V_m (%)‡
10% Waste, 5% Sewage, 85% Water								
0	10	285	49	198	139	4.78	0.79	90
2		285	45	218	123	5.92	0.80	90
4		285	39	214	105	6.52	0.81	90
6		285	34	234	84	7.30	0.77	91
20% Waste, 5% Sewage, 75% Water								
0	20	560	63	542	109	4.38	0.79	88
5		560	48	610	90	5.41	0.86	88
10		560	28	605	72	6.39	0.84	91
15		560	29	790	133	7.46	0.87	90
20% Waste, 5% Sewage, 75% Water								
0	30	560	50	560	83	4.37	0.72	88
3		560	49	534	84	4.86	0.77	88
6		560	40	551	89	5.84	0.83	89
9		560	31	615	72	6.45	0.74	89

* A nitrogen deficiency existed in all cases.
† Sludge volume index (Mohlman).
‡ Volatile matter.

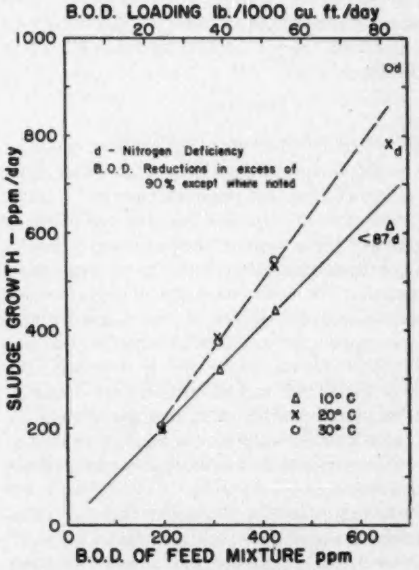
B.O.D. LOADING lb./1000 cu. ft./day
SLUDGE GROWTH - ppm/day
B.O.D. OF FEED MIXTURE ppm
d - Nitrogen Deficiency
B.O.D. Reductions in excess of 90% except where noted
Δ 10° C
X 20° C
O 30° C

FIG. 2. *Activated sludge growth* vs. *B.O.D. loading.*

Nitrogen and Phosphorus Requirements

Nitrogen requirements are shown in Table VIII. The requirements computed on the basis of sludge growth are in good agreement with those computed from influent-effluent analyses. The nitrogen requirement (or in this instance, nitrogen utilized) increased with an increase in supplementary nitrogen, as might be expected; but the highest requirements in run E did not quite reach the maximum requirements as determined in run C. These data reinforce the conclusion that a nitrogen deficiency existed in all instances during run E.

Phosphorus requirements are shown in Table IX. A very slight increase in the phosphorus requirement occurred with increases in supplementary nitrogen. The phosphorus requirements in this run were considerably lower than those in run C. The lower values were the result of slower rates of sludge growth caused by the nitrogen deficiency and lower sludge phosphorus contents. The reasons for the lower phosphorus contents in run E are not known.

Nutrition and Process Efficiency

Some of the effects of nitrogen deficiencies on the activated-sludge process are illustrated in Table X. As the magnitude of nitrogen deficiencies became less, the B.O.D. of the effluents and the sludge volume indices improved and the rates of sludge growth and sludge nitrogen contents increased.

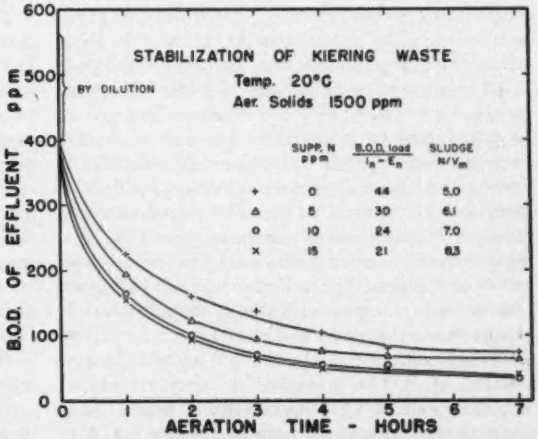

FIG. 3. *Effect of available nitrogen on rate of B.O.D. removal.*

TABLE XI. AVAILABILITY OF ORGANIC NITROGEN FROM COTTON KIERING WASTE
(PERCENTAGE OF ORGANIC N UTILIZED FROM WASTE)

Temp. (°C)	Run C		Run E
	Sewage	Waste	Waste
10	72	21	27
20	71	45	57
30	77	70	54

The variation in sludge nitrogen content was considerable, ranging from 4.38% to 7.46% at 20°C.

The sludge phosphorus contents, on the other hand, were not affected appreciably by the increase in supplementary nitrogen. Since the rate of sludge growth was a variable, a likely explanation for the constant phosphorus content is that the maximum phosphorus requirements of the sludge were being satisfied.

A qualitative observation made during the course of the experiments was that the greater the magnitude of the nitrogen deficiency, the more difficult the sludges were to dewater. This effect would be of importance in a plant using vacuum filtration of excess sludge.

In order to investigate the effects of a nitrogen deficiency on B.O.D. removal, samples were taken for B.O.D. analysis several times during an aeration period. The results of one of these tests at 20°C are plotted in Figure 3. The effect of a nitrogen deficiency was to decrease the rate of B.O.D. removal considerably. For example, the B.O.D. was reduced to 100 p.p.m. in about 2 hrs. when 10 p.p.m. supplementary nitrogen was added, while over 4 hrs. were required to reduce the B.O.D. to this same value when no supplementary nitrogen was added.

An important point to note in Figure 3 is that increasing the supplementary nitrogen from 10 to 15 p.p.m. had little effect on the rate of B.O.D. removal even though a nitrogen deficiency still existed at 15 p.p.m. supplementation. Evidently, using B.O.D. removal as the criterion, the critical nitrogen requirement is somewhat less than the maximum nitrogen requirement. On the basis of curves of the same type as Figure 3, critical nitrogen requirements of activated sludge in the stabilization of cotton kiering waste using 1500 p.p.m. aeration solids were estimated to be 3.3, 4.2, and 4.2 lbs. per 100 lbs. of B.O.D. stabilized at temperatures of 10°, 20°, and 30°C, respectively. These values compare with maximum requirements of 5.6, 6.2, and 6.2 lbs. per 100 lbs. of B.O.D. stabilized.

Availability of Organic Nitrogen

The limited availability of the organic nitrogen contained in the waste being stabilized has been pointed out. In order to determine more exactly what portion of the organic nitrogen does become available, calculations were made based on the influent and effluent analyses. The results are given in Table XI. The organic-nitrogen availabilities in runs C and E are comparable; however, the availability of the kiering waste organic nitrogen was appreciably less than the availability of the run C sewage organic nitrogen. The effect of increasing the temperature was to increase the availability.

Nutritional Requirements of Trickling Filters

It is to be anticipated that questions will be raised concerning the application of data obtained by means of activated sludge to trickling filters. Such studies have been made by Kilgore [6] on three industrial wastes, including kiering waste. His conclusion was "the nutritional requirements of high-rate trickling filters and of the activated-sludge process are similar." As with the activated-sludge studies, his work has shown that satisfactory stabilization can be obtained when moderate deficiencies occur at normal B.O.D. loadings of 50 to 70 lbs. per 1000 cu. ft. of filter, provided adequate recirculation is used.

Discussion

Calculations Based on Nutritional Studies

The results of runs C and E have provided additional evidence that the presence of certain nutritional elements is essential for the satisfactory functioning of the activated-sludge process. Nitrogen and phosphorus requirements can be determined experimentally, or even calculated if certain basic data concerning the nature of the substrate and stabilization process are available. The balance method of calculation can be used to determine the amount of waste that can be treated with domestic sewage without resulting in a nitrogen deficiency or, in cases where insufficient sewage is available, to determine the amount of supplementary nutrients required.

The basic data required in order to make these calculations are as follows: sewage and waste characteristics—B.O.D., total nitrogen, organic nitrogen (amount and availability); process variables—temperature, concentration of aeration solids, aeration

time. The effects of other aeration periods and concentrations of aeration solids were not considered in this work.

Solutions for two situations can be obtained by using equation (1):

1. Estimation of limiting industrial-waste load for municipal plants.—For the situation in which cotton kiering waste is treated in mixture with sewage, the limiting concentration of waste without the creation of nitrogen deficiency is reached when the value E_n approaches zero or is represented only by organic nitrogen. For a given sewage-waste mixture, the term I_n is known, the critical E_n can be estimated from the organic-nitrogen availability data, and the growth, G, can be determined by using Figure 2. The sludge nitrogen content, N, can then be calculated by using equation (1). The results of run C indicate that a nitrogen deficiency is likely to be encountered if the calculated value of N is less than 8. By the assumption of several waste-sewage mixtures, the limiting concentration of waste can be found by trial.

2. Estimation of supplementary nitrogen required for the stabilization of a waste-sewage mixture deficient in available nitrogen.—For the stabilization of kiering waste without the benefit of a sufficient quantity of sewage to supply nitrogen requirements, values for E_n and G can be found as above. A value for N of 8% could be assumed, but data of run E indicate that moderate nitrogen deficiencies may exist without appreciable reduction in rate of B.O.D. removal. Significant reduction in rates of removal did not occur until the sludge nitrogen had fallen below 6.5%. Therefore, the use of this figure seems preferable to the value of 8%.

The required influent nitrogen, I_n, can be found by using equation (1). When the amount of available nitrogen contained in the waste and small amount of sewage is subtracted from the calculated I_n, the result represents additional nitrogen required.

Interpretations Based on Nitrogen Content of Sludge

The nitrogen content of the activated sludge would appear to be a reasonable indication of whether or not an activated-sludge plant is being operated with sufficient available nitrogen. If difficulties are believed to be caused by a deficiency of nitrogen, a fast diagnostic method for determining whether or not this hypothesis is correct is to determine the nitrogen and volatile-matter content of the sludge. The rate of B.O.D. reduction in run E did not decrease appreciably until the value for N/V_m fell below 7, and this value would appear to be a useful criterion for diagnosis.

A sludge analysis should prove to be a better diagnostic tool than an analysis of the effluent for inorganic nitrogen. An effluent devoid of inorganic nitrogen indicates a nitrogen deficiency, but does not measure the magnitude of that deficiency. Operation at a slight deficiency could not be controlled by effluent analyses, but control could be attained using sludge analyses.

Phosphorus Requirements

Because phosphorus deficiencies were not encountered in either run, the nitrogen balance has been emphasized in the foregoing study. However, the same approach should be applicable to the study of either nitrogen or phosphorus requirements.

Summary and Conclusions

The following conclusions are based on laboratory studies concerning the stabilization of domestic sewage-cotton kiering waste mixtures by activated sludge. Conditions of treatment were a 7-hr. aeration period, 1500 p.p.m. aeration solids, and temperatures controlled at 10°, 20°, and 30°C.

1. At 20° and 30°C, up to 20% cotton kiering waste of the type used can be treated successfully in mixture with Boston sewage without marked impairment of the stabilization process. With 20% waste in the mixture, a nitrogen deficiency occurred at all temperatures, but the only impairment of B.O.D. reduction occurred at 10°C.

2. Results also indicate that cotton kiering waste can be treated successfully in mixture with as little as 5% sanitary sewage and with B.O.D. loadings as high as 35 lbs. per 1000 cu. ft. aeration capacity at 10°C and 70 lbs. per 1000 cu. ft. at 20° and 30°C if the nitrogen requirements are supplied by supplementation.

3. Maximum nitrogen requirements, as determined with domestic sewage-kiering waste mixtures, were 5.6, 6.2 and 6.2 lbs. per 100 lbs. of 5-day B.O.D. removed at 10°, 20°, and 30°C, respectively. Maximum phosphorus requirements under similar conditions were 1.0, 1.2, and 1.1 lbs. per 100 lbs. of B.O.D. removed.

4. Critical nitrogen requirements, on the basis of B.O.D. removal, are estimated to be 3.3, 4.2, and 4.2 lbs. per 100 lbs. B.O.D. removed at 10°, 20°,

and 30°C, respectively. The maximum phosphorus requirements under these conditions which involved nitrogen deficiencies were 0.4, 0.5, and 0.5 lb. per 100 lbs. B.O.D. removed at 10°, 20°, and 30°C.

5. A nitrogen deficiency tends to decrease the rate of B.O.D. removal and to impair the settling and dewatering characteristics of the sludge.

6. Nutritional requirements of activated sludge are directly related to the amount of sludge growth.

7. At a given temperature and with an excess of nutrients, the rate of activated-sludge growth is directly proportional to the B.O.D. stabilized.

8. The percent nitrogen content of dried activated sludge based on volatile matter is a good index of nitrogen deficiencies. A value of less than 7% is indicative of a critical deficiency.

9. Cotton kiering waste of the type used will not, in general, require supplementation with phosphorus in order to be treated successfully by activated sludge.

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Synthetics in Cotton Detergency

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ALTHOUGH the first modern synthetic surface-active agents (also called "surfactants" or "syndets" for abbreviation) were produced in 1917, the growth of this new industry was relatively slow until the close of World War II. After 1946 the production curve rose sharply, as shown in Figure 1.† One of the major factors contributing to this spectacular postwar growth has been the rapid public acceptance of these products for household use; it has been reported that over half of the surfactant production of this country is currently going into packaged household detergents.

Initially, surfactants or syndets had been developed as textile-processing auxiliaries and later found limited domestic use as dishwashing or fine-fabric detergents. It was generally believed that the synthetics could not compete with soap and soap products for use in household laundering—*i.e.*, in cotton detergency. The shortcomings of the synthetic detergents in this field were vaguely ascribed to a lack of "colloidality" and poor suspending power of their solutions. About 1945, however, reports of German work on the building of synthetics with carboxymethylcellulose started to appear [3], and for the first time possibilities of synthetic detergents for home laundering were seriously considered. Due to the great economic importance of this appli-

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† The authors are indebted to Mr. W. H. Healey of General Dyestuff Corp. for the data shown in Figure 1. A more recent estimate was published by Snell [13].

TABLE I. LAUNDER-OMETER TEST DATA

Detergent	Reflectance (%) after washing* Run A	Run B
IV	42	45
I	41	41
III	40	38
II	34	35

* Initial reflectance = 16% for all swatches.

cation, a number of industrial laboratories in the U. S. initiated research programs along this line. This led also to a re-examination of some long-accepted concepts related to the mechanism of detergency—the experiences at this laboratory providing a case in point.

Laboratory Testing Methods

In the early stages of General Aniline's development program, emphasis was placed on the procedure described by Harris [2], which involved soiling the cotton with a suspension of Oildag and Wesson Oil in carbon tetrachloride, then washing in a Launder-Ometer, and grading by a conventional reflectometer. Typical results obtained in duplicate runs with a group of four detergents are shown in Table I. The wash tests were carried out in tap water at 140°F containing 0.25% of the following built or diluted compounds: *I*, a built nonionic detergent (15% Antarox A-200 plus carboxymethylcellulose and alkalies); *II*, a built household soap powder (about 65% soap); *III*, a 15% solution of the nonionic built with carboxymethylcellulose only; *IV*, a 15% solution of the nonionic detergent alone.

As can be seen from Table I, where the compounds are listed in decreasing order of their apparent effectiveness, the unbuilt nonionic agent alone (*IV*) performed better in this test than either of the two built synthetic detergent compositions (*I* and *III*) or soap (*II*). While somewhat similar results reported by Armstrong *et al.* [1] confirm the outcome of the present evaluation, the findings appear contrary to practical experience; in practice, synthetic detergents were not found to perform well when applied without suitable builders.

The same group of detergents were also evaluated using four different types of commercially available soiled test fabrics, the soil in all cases being predominantly carbon black, lampblack, or graphite. The test cloths, identified here by letters *A–D*, were received from the following sources: *A*, General Dyestuff Corp. (Test Fabric No. 26); *B*, U. S. Testing Co., Inc.; *C*, American Conditioning House, Inc.; *D*, Foster D. Snell, Inc.

Typical reflectance values obtained by washing the various fabrics in a Terg-O-Tometer, under conditions otherwise the same as those described above, are summarized in Figure 2. The average initial reflectance level of each type of cloth is indicated below the respective blocks. In each block the detergents, represented by bars, were arranged in decreasing order of their apparent effectiveness, and, as can be seen, the unbuilt detergent (*IV*) appeared poorest in all cases (as it should). However, conflicting results were still encountered since the built detergent (*I*) appeared superior to soap (*II*) in the tests with cloths *C* and *D*, but appeared inferior in the tests with cloths *A* and *B*. Similarly conflicting results were reported by Merrill and Getty [7], who tried to evaluate synthetic detergent-alkaline builder mixtures by washing two commercial soiled test fabrics of the types identified here as cloths *B* and *D*.

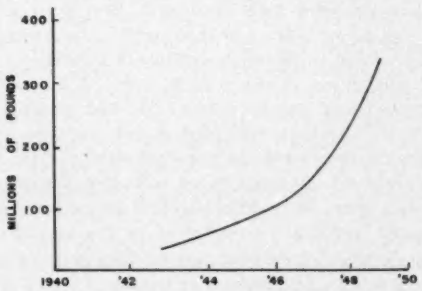

FIG. 1. *Surfactant production.*

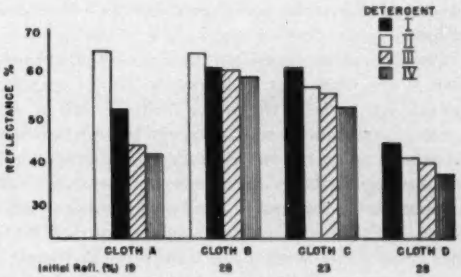

FIG. 2. *Terg-O-Tometer wash tests with commercial test fabrics.*

Major Limitations of Testing Methods

While recent reviews of testing methods [12] and their limitations [6] refer to many factors that could lead to contradictory results, it was concluded that the detergency tests as performed here suffered from two major drawbacks: the type of soil used, and the nature of the washing process.

In the first place, the very heavy deposits of finely divided carbon commonly used are not representative of normal soil. The larger part of this carbon is deposited rather loosely between threads and on fibers, whereas a smaller (and more significant) portion penetrates deeply into the fiber structure where it is held tenaciously by solid-solid adhesion forces existing between the carbon surface and the cellulose and, to a lesser extent, by mechanical entrapment. During normal Launder-Ometer washing operations, the more superficially held carbon is removed fairly readily, leaving the ingrained soil behind. The extent to which different detergents remove this superficial carbon from various "standard" soiled cloths varies somewhat, depending upon such factors as the degree of flocculation of the carbon, type of carbon, humidity during soiling, dispersing power of the detergent, etc. However, removal of as much as 95% of the carbon will leave a grey cloth, and it is the residual ingrained soil (which is left untouched in conventional wash tests) that is most significant in practical laundering, where whiteness is the goal. In short, tests with heavily carbon-soiled swatches measure only the removal of superficial, rather than ingrained, soil. Real soil usually does contain some finely divided carbon (soot), but the particles are intimately associated with siliceous and other materials, so that the cellulose-carbon adhesion is weakened. In addition, the amount of carbonaceous soil present is much lower than in laboratory soiling.

The second weakness of the conventional wash test is the fact that redeposition is not usually considered. One of the major contributions of the carboxymethylcellulose, according to the German reports, is in preventing redeposition of suspended soil during washing and rinsing. The extent of redeposition is normally small for a single wash; hence, multiple soilings and washings, rather than the usual single wash cycle employed in conventional tests, would be required to expose this factor. Practical laundering, of course, involves a series of soil-wash cycles.

A More Realistic Testing Method

As a result of reasoning of this sort, a new type of cotton-detergency test was developed in this laboratory, which is described in detail elsewhere [10]. In brief, it consists of the following steps: A realistic synthetic soil was formulated, based on analyses of floor sweepings from various cities. This comprises a mixture of siliceous, earthy, and oily materials, with minor amounts of carbon black. This soil is applied dry to cotton by rubbing with a modified Schiefer abrasion meter. An after-treatment with a moist abradant plate simulates perspiration. The soiled swatches are washed in a Terg-O-Tometer and are then resoiled and rewashed for a number of cycles in order to slowly build up an accumulation of unremoved and redeposited soil in a realistic fashion.

Using the above technique, results were obtained with the four detergent systems described above which indicated that *I* was equal to but not better than *II*, and that *III* and *IV* were decidedly inferior. This rating seems to correlate well with practical field tests that had been performed independently.

Continuation of work along these lines finally led to the conclusion that the synthetic detergents could be built to perform at least as well as soap for cotton detergency. The tremendous volume of heavy-duty synthetics being used by housewives today confirms this in a very practical way.

Mechanism of Building Action

In spite of this proved effectiveness of builders such as polyphosphates and carboxymethylcellulose, very little is actually known about the underlying mechanism of the building action.* It is true that alkaline builders, such as silicates, have been used with soaps for years, but their action was assumed to be related to the neutralization of acid soils and the prevention of soap hydrolysis. The results described here can hardly be explained so simply, since the synthetic soil used is not acid and the synthetic detergents do not hydrolyze. Prior to the discovery of carboxymethylcellulose, the use of alkalies alone as builders for synthetics had also received considerable treatment in the literature, where it was claimed that most alkalies improve the detergency of the alkylaryl sulfonates.

* A comprehensive discussion of builders in detergency was recently given by Niven [8].

TABLE II. DETERGENCY VS. SURFACE ACTIVITY

Detergent	Reflectance (%)	Surface tension (dynes/cm.)	Interfacial tension (dynes/cm.)	Wetting (sec.)	Solubilization (mg. dye/100 ml. soln.)
Nonionic	58.8	30	3	27	1.3
+ TSPP*	60.0	30	3	26	1.7
+ CMC†	62.5	30	3	25	1.3
+ (TSPP, CMC)	65.0	30	3	26	1.5
Alkylaryl sulfonate	44.3	28	2	24	0.3
+ TSPP	58.8	27	3	30	0.6
+ CMC	52.3	30	2	27	0.3
+ (TSPP, CMC)	62.0	27	2	25	0.7

* Tetrasodium pyrophosphate.
† Carboxymethylcellulose.

In an attempt to shed some light on the mechanism of building action, a series of experiments were carried out using the new test method with both a nonionic and an alkylaryl sulfonate; the results are shown in Table II. The two detergents (at 0.05% concentration) were built with tetrasodium pyrophosphate (0.1%) and carboxymethylcellulose (0.01%), both separately and together. As can be seen, the detergency of the nonionic is not improved much by alkali, whereas that of the alkylaryl sulfonate is greatly increased, in agreement with the literature. Building with CMC alone also appears to improve detergency, but again the effect is greater for the alkylaryl sulfonate. Finally, building with both alkali and CMC gave the best results of all.

One of the theories frequently advanced to explain the action of builders is that they influence the surface activity of the detergent. To test this, surface tension, interfacial tension (against Nujol), wetting (Draves test), and dye solubilization were determined, using the eight systems in Table II. The latter test was performed according to a simplified method described by Lambert and Busse [5], and the values shown represent mg. dye/100 ml. detergent solution. As can be seen, none of these variables was significantly affected by the presence of the builders, except perhaps for a slight rise in solubilization on adding alkali. However, there appears to be no correlation between solubilization and detergency. It is believed safe to conclude that the beneficial effect of builders is not due to any change in the surface activity of the detergent.

The alkali can conceivably act in a number of other ways, such as by swelling the fiber interstices, entering into ion-exchange with the soil components, or influencing the degree of adsorption of the synthetic by the fiber. The major role of the alkali might be to increase the negative charge on both the fiber and the soil through adsorption of the anions, thus helping to break the adhesive bond between soil and fabric through an electrostatic or *zeta*-potential effect. A somewhat related action has been observed in the case of mechanical dishwashing [11] where a foodstuff suspension was sprayed onto glass slides in a dishwashing machine and the adherence determined by a gloss measurement. With no alkali or surfactant present, a reading of about 71 was obtained; with small amounts of pyrophosphate present, the adherence of food particles was reduced, the gloss rising to about 83. It is believed that adsorption of the alkali anion is responsible. Powney and Noad [9] have published similar data for the adherence of ilmenite to cotton.

As for the action of carboxymethylcellulose, there are indications that the major factor involved is the adsorption of the CMC onto the cotton itself. British workers [4] have found that fixation of CMC onto the cotton by acid treatment produces a resistance to wet soiling; the present authors have noted a similar effect using carboxymethylated cotton from the Southern Regional Research Laboratory.

Detergency of Carboxymethylated Cotton

These tests were carried out by soiling the carboxymethylated cloth and an untreated control with the composite synthetic soil described, using both the "dry" method developed in this laboratory [10] and aqueous suspensions of the soil. Washings of the soiled swatches were carried out using a built nonionic detergent. As can be seen from Table III, the carboxymethylated cloth showed a definite resistance to soiling by "wet" or suspended dirt.

TABLE III. EFFECT OF CARBOXYMETHYLATION ON SOIL-RESISTANCE

System	Average reflectances (%) After soiling	After washing
"Dry" soiling		
Untreated cloth	25	42
Carboxymethylated cloth	26	41
Wet soiling		
Untreated cloth	46	54
Carboxymethylated cloth	53	61

As was expected, this cloth could not resist the dry soiling because of the nature of the process, which consists of rubbing the soil into the fabric. On washing, it was rather surprising that about the same amount of dirt was removed from both the treated and untreated cloths. The explanation may be that the carboxymethylation prevents some of the finer soil particles from penetrating deeply into the fabric (by mechanically blocking the interstices) but such soil as does adhere is not removed any more readily than from unmodified cotton.

In addition, it has been noticed that cotton swatches that had once been washed in detergents containing CMC were thereafter difficult to resoil from aqueous suspensions of dirt, the character of the cotton apparently having been changed. It would seem logical to assume that the CMC acts by being adsorbed onto the cotton, mechanically blocking the finer capillaries or interstices in the fiber, and thus preventing penetration of the extremely fine soil particles.

While the above mechanism would seem to apply more to redeposition of soil than to soil removal, the two are rather difficult to separate completely in practice. Thus, the unbuilt alkylaryl sulfonate showed considerable redeposition during washing, as could be seen by the greying of unsoiled portions of the swatch. The apparent improvement in detergency on adding CMC is perhaps due mostly to prevention of this redeposition rather than to any actual increase in soil-removing power.

Summary

It appears fairly certain that synthetic detergents can be built with phosphates and CMC so as to wash cottons about as well as soap does. Although the mechanism of building action is very complex, it may be attributed, at least in part, to: adsorption of the phosphate ion, which modifies the charges on soil and fabric; and a mechanical blocking action of CMC at the fiber interstices.

Acknowledgment

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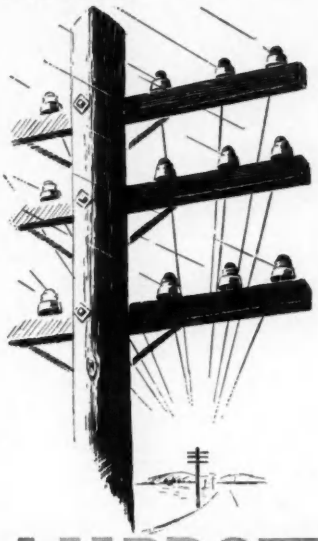

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